

Jimma University
College of Natural Sciences
Department of Chemistry



Continuing and Distance Education Programme
Module for
Industrial Chemistry II (Chem 451)

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August, 2011
Jimma, Ethiopia

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1 Title page

9 pages: including Copy right, Module overview, Table of contents and self study time

196 Module main body pages: including Chapter summaries and Self test exercises

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General Introduction to the module

Industrial Chemistry deals with commercial production of chemicals and related products from natural raw materials and their derivatives. It enables humanity to experience the benefits of chemistry when we apply it in the exploitation of materials and energy. When we apply chemistry in the transformation of materials and energy to make useable products. This results in growth and improvement in areas such as food production, health and hygiene, shelter and clothing. The economic growth of industrialized countries relies on the manufacturing industry for finished products. The goal of studying industrial chemistry II at university is to try and bridge the gap between classical Chemistry and Chemistry as applied in industry.

The Chemical industry is highly globalized and produces thousands of chemicals from a wide variety of raw materials by means of varied technologies for varied end uses. It is therefore, important to base the study of Industrial Chemistry on an understanding of the structure of the industry and the unit operations and unit processes that make up the chemical processes.

Different basic organic products can be prepared through industrial organic synthesis turning now to organic chemical industry; we use petroleum as the source of petrochemicals and synthetic polymers. Fermentation enables us to convert natural organic materials into chemicals, some like penicillin being pharmaceutical ingredients. From natural oils and fats, we obtain soaps and detergents. Insecticides are agents of chemical or biological origin that control insects. Control may result from killing the insect or otherwise preventing it from engaging in behaviors deemed destructive.

Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance. The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied. Leather can be produced through different manufacturing processes, ranging from cottage industry to industry. Leather is made from animal skins or hides which have been chemically treated to preserve quality and natural beauty.

Overview of the module

This module starts with coal and petroleum processing. It further discuss about the origin of coal and its ranking, petroleum origin, classification and mining, distillation of petroleum, rating of Petrol and Diesel, how Cracking, Alkylation, Hydrotreating and reforming are used in petroleum processing. The second chapter discusses how Petrochemicals are manufactured from Methane, Ethylene, Propylene, Butylenes and Benzene, Toluene, Xylene (BTX) and Manufacture of Acetylene, Ethylene oxide, Acrylonitile, Dimethyl terephthalate

The third chapter deals how basic Organic chemicals such as Methanol and Isopropanol, Formaldehyde and Acetaldehyde, Acetic acid, Acetone, Phenol and Styrene are synthesized industrially. The fourth chapter discusses with polymers, Plastics, Methods of Polymerization, Properties and classification of plastics, Effect of polymer structure on properties, Properties and classification of rubber, Properties and classification of fibers. The fifth chapter deals how sucrose or sugar is manufactured from sugar cane and sugar beet. The sixth chapter deals with properties, classification and manufacture of Oils, Fats and Detergents.

The seventh chapter discusses with Pulp and Paper Industry. It elaborates how pulp and paper are manufactured by mechanical, thermomechanical and chemical process. The eighth chapter discusses how chemical food stuff is processed. It discusses how Alcoholic beverages, such as Beer, wine, distilled Spirit and Soft drinks are manufactured industrially. The ninth chapter deals with Pharmaceutical Industry. It discusses the Discovery and development of drugs, Classification and the Chemistry of pharmaceutical products, Manufacturing of pharmaceutical products and Quality Control of Pharmaceuticals.

The tenth chapter deals with Chemicals for Agriculture. It discusses some of the chemicals such as Insecticides, DDT, BHC and Parathion, Fungicides and 2,4,6-Trichloro Phenol, Herbicides–2,4-D and 2,4,5–T, Pesticides pollution in Agricultural activities. The eleventh chapter discusses what Dyestuff is. It elaborates about Dyes, Color and Constitution, Methods of dyeing and Classification of dyes. The module closes with the study of Leather Industry; how hides are prepared for tanning, Leather Tanning and Leather production processes, Vegetable tanning, Chrome tanning, Leather finishing, Role of enzymes in leather production, Environmental impacts of Leather Industry.

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Mode of delivery: Tutorial, group discussion, group and individual assignment.

Mode of assessment: Quizzes, assignments, tests, and final examination.

Mode of evaluation:

Assignment	30%
Final exam	70%
Total	100%

Reference materials:

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Self study time of the module

This unit will require 170 hours

The following table is your study time table

Module and contents	Study time(Hours)	Duration
1. Coal & petroleum processing	20	Tikimit 1-30, 2004 E.C
2. Main petrochemicals	10	Hidar 1-15, 2004 E.C
3. Basic organic products	10	Hidar 16-30, 2004 E.C
4. Plastics, Rubber and Fibers	25	Tahsas 1-30, 2004 E.C
5. Sucrose industry	10	Tir 1-15, 2004 E.C
6. Oils, Fats and Detergents	15	Tir 20- Yekatit 10, 2004 E.C
7. Paper Industry	15	Yekatit 11- Yekatit 30, 2004 E.C
8. Chemical Food stuff processing	15	Megabit 1- Megabit 20, 2004 E.C
9. Pharmaceutical Industry	15	Megabit 25- Miazia 15, 2004 E.C
10. Chemicals for Agriculture	10	Miazia 20- Ginbot 5, 2004 E.C
11. Dyestuff	10	Ginbot 6- 20, 2004 E.C
12. Leather Industry	15	Ginbot 21- Sene 10,2004 E.C
Total	170	



Unit Introduction

Dear student, this chapter deals with coal and petroleum processing. It deals with definition of some basic terms, which provide you the basic concept of coal and petroleum processing. We will also discuss further about the origin of Coal and its ranking, Gasification of coal, hydrogenation of coal, Petroleum origin, classification and mining, distillation of petroleum, rating of Petrol and Diesel, Cracking, alkylation, Hydrotreating and reforming in petroleum processing.



Learning objective of the unit





Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:-

- Define important terms like Coal, carbonization of coal, gasification of coal, hydrogenation of coal, petroleum oil, and distillation of petroleum oil
- Mention some of the origin and common ranking of coal
- Give examples for classification of petroleum
- Explain the difference between carbonization and gasification of coal
- Compare and contrast the rating of Petrol and Diesel
- Explain the difference among Cracking, Alkylation, Hydrotreating and Reforming in petroleum processing/refinery

1.1 Coal; *its origin and its ranking*

Dear student, under this main content you learn about the origin of coal and its ranking. Do you know what a coal is, its origin and ranking? Let warm up your self with the following activities.

	Learning task 1.1	
<ul style="list-style-type: none">a. Define Coalb. Explain how coal is formedc. List the major composition of coald. List the common ranking of coale. Mention the major uses of coal		

Coal is a readily combustible black or brownish-black sedimentary rock normally occurring in rock strata in *layers or veins* called **coal beds**. The harder forms, such as anthracite coal, can be regarded as metamorphic rock because of later exposure to elevated temperature and pressure. It is formed from mineralized vegetative material deposited over a long period of time partial decayed (altered chemical composition) resulting from increased Temperature and Pressure and restricted access to oxygen. There are different factors for coal formation. The major factors rely on three factors. These are:

1. Initiation, maintenance, and repetition of environments that favor large-scale accumulation and preservation of vegetal sediment;
2. Conditions within this depositional environment that favor biological degradation and alteration of the vegetal sediment to peat [peatification]; and
3. Geochemical processes that induce chemical coalification of the peat to higher-rank coal.”

Coal primarily consists of Carbon (> 50%) where other components such as volatile matter, Sulphur, Chlorine, Phosphorus, Nitrogen and trace amount dirt and other elements exist as impurities. Coal is extracted from the ground by mining, either underground or in pits. Coal, a fossil fuel, is the largest source of energy for the generation of electricity worldwide, as well as one of the largest worldwide anthropogenic sources of carbon dioxide emissions. For example,

the gross carbon dioxide emissions from coal usage are slightly more than those from petroleum and about double the amount from natural gas.

There are different types of Coal. Such types of coals are formed because of geological processes apply pressure to dead biotic material over time, under suitable conditions it is transformed successively into the following types of coal. The main ones are:

i) Peat, considered to be a precursor of coal, has industrial importance as a fuel in some regions. In its dehydrated form, peat is a highly effective absorbent for fuel and oil spills on land and water.

ii) Lignite, also referred to as brown coal, is the lowest rank of coal and used almost exclusively as fuel for electric power generation. Jet is a compact form of lignite that is sometimes polished and has been used as an ornamental stone since the Iron Age.

iii) Sub-bituminous coal, whose properties range from those of lignite to those of bituminous coal is used primarily as fuel for steam-electric power generation. Additionally, it is an important source of light aromatic hydrocarbons for the chemical synthesis industry.

iv) Bituminous coal, dense mineral, black but sometimes dark brown, often with well-defined bands of bright and dull material, used primarily as fuel in steam-electric power generation, with substantial quantities also used for heat and power applications in manufacturing and to make coke.

v) Steam coal is a grade between bituminous coal and anthracite, once widely used as a fuel for steam locomotives. It is used as a fuel for domestic water heating.



vi) Anthracite, the highest rank; a harder, glossy, black coal used primarily for residential and commercial space heating.

vi) Graphite, technically the highest rank, but difficult to ignite and is not so commonly used as fuel: It is mostly used in pencils and, when powdered, as a lubricant.

The classification of coal is generally based on the **content of volatiles**. However, the exact classification varies between **countries**.

1.1.1 Carbonization of coal

Dear student, in the previous content, you have introduced that the origin of coal and its ranking. Now you learn about carbonization of coal and its advantage. Let warm up yourself with the following activities.



	Learning task 1.1.1	
a) Define carbonization of coal. b) Explain the advantage of carbonization of coal?		

Carbonization is the term used for the conversion of an organic substance into carbon (Coke) and liquid and gaseous carbon-containing residues (coal gas and coal tar) through pyrolysis or destructive distillation. Coke produced by this process is used in the iron and steel industry and as a domestic smokeless fuel. With little exception only coals in bituminous rank are limited to produces acceptable metallurgical cokes.

A significant development in understanding carbonization processes was made with the discovery of mesophase in the plastic stage of carbonization leading to graphitizable carbons, as observed by optical microscopy. Essentially during the carbonization process *dehydrogenative polymerization of aromatic molecules occurs*, with a consequential increase in average molecular weight. The final coke structure is related to the properties of mesophase at the time of solidification and these, in turn are dominantly dependent upon the chemical properties of the parent material.

1.1.2 Gasification of coal

Dear student, in the previous content, you have introduced that how a coal is carbonized. Now you learn about Gasification of Coal. Do you know what Gasification is? Let warm up your self with the following activities.

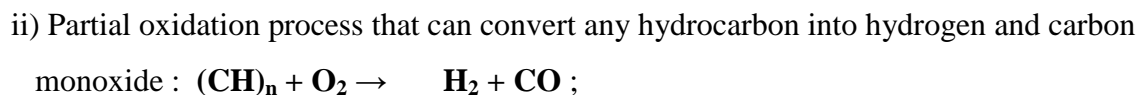
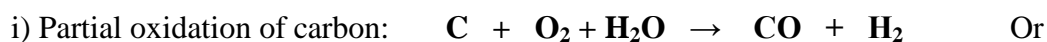
	Learning task 1.1.2	
a) Define Gasification of coal		
b) Mention some of the major products produced during gasification of coal		
c) Explain the advantage of gasification of coal		

Coal gasification is the process of producing coal gas or "synthesis" gas (syngas) (which is a mixture of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂) and water vapour (H₂O) from coal. A mixture of carbon monoxide (CO) and hydrogen (H₂) gas is called can be used to produce Syngas can then be converted into transportation fuels like gasoline and diesel through the Fischer-Tropsch process.

Alternatively, the hydrogen obtained from gasification can be used for various purposes such as powering a hydrogen economy, making ammonia, or upgrading fossil fuels. During gasification, the coal is mixed with oxygen and steam (water vapor) while also being heated and pressurized. During the reaction, oxygen and water molecules oxidize the coal into carbon monoxide (CO) while also releasing hydrogen (H₂) gas. This process has been conducted in both underground coal mines and in coal refineries. **Note: Gasification is not combustion**



Syngas can also be produced from:-



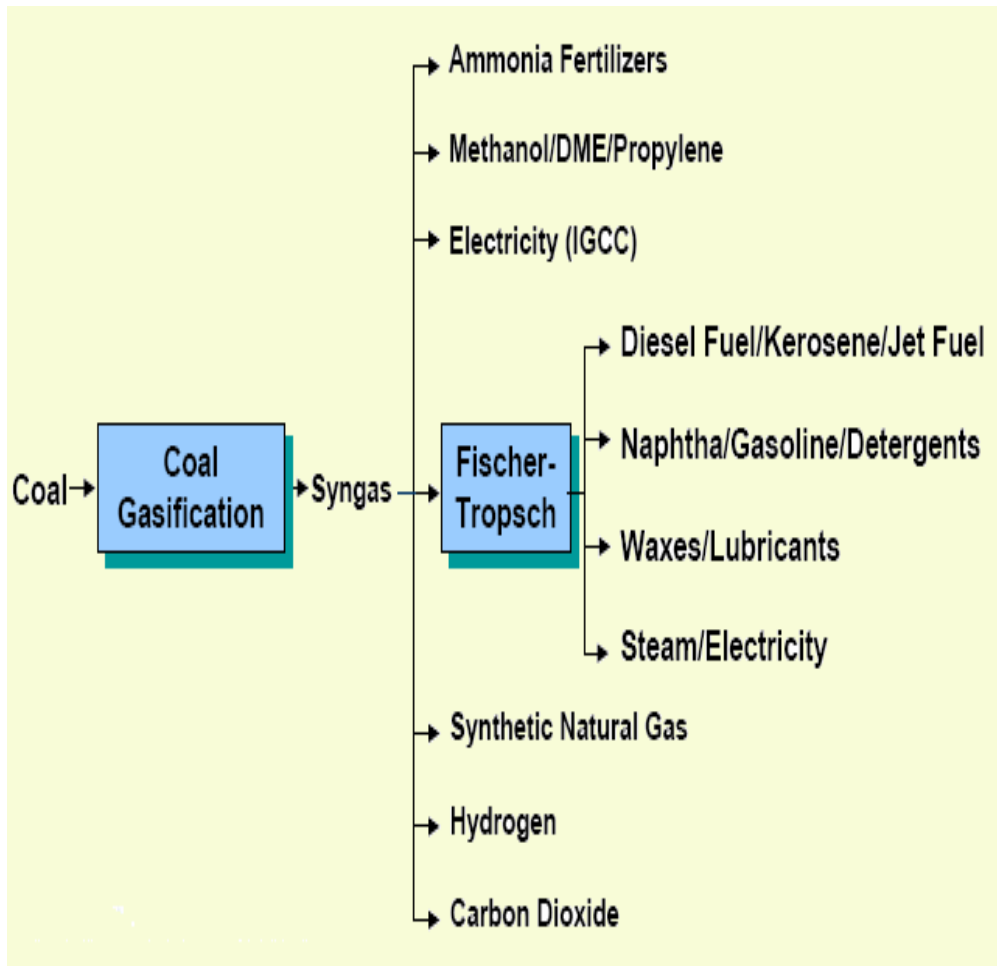




Figure 1.1.2 Gasification of coal and its products

Dear student, why a coal is gasified?

As stated before, Coal gasification is used to produce syngas and it is the cleanest coal technology. This is because of inherently lower SO_x, NO_x, particulate matter, collateral solid wastes and wastewater. The method can also provide cost effective removal of mercury and sequestration of CO₂.

1.1.3 Liquefaction of coal

Dear student, in the previous content, you have introduced that how a coal is gasified, now you learn about hydrogenation of coal. Do you know Hydrogenation? Let warm up your self with the following activities.

	Learning task 1.1.3	
a) Define hydrogenation of coal		
b) Mention some of the major products obtained during hydrogenation of coal		

1.1.3.1 Hydrogenation of coal

Hydrogenation of coal is direct conversion of coal to liquids. One of such process called “**Bergius process**” developed by Friedrich Bergius in 1913 dry coal is mixed with heavy oil recycled from the process. The mixture is kept between 400 °C (752 °F) to 5,000 °C (9,030 °F) and 20 to 70 MPa hydrogen pressure in the presence of catalyst for the following reaction to:



1.1.3.2 Fischer-Tropsch process

Fischer-Tropsch process is an indirect processes used to convert the syngas into light hydrocarbons (like ethane) in the presence of Fischer-Tropsch catalysts. Ethane produced here is further processed into gasoline and diesel. The method was used on a large technical scale in Germany between 1934 and 1945 and is currently being used by different countries. Coal liquefaction methods involve carbon dioxide (CO₂) emissions in the conversion process. Different liquefaction processes have different lifecycle carbon footprints depending on which processes and environmental controls are employed.

Dear student, do you believe that coal mining can have environmental effects?

1.1.4 Environmental effects of Coal mining

There are a number of adverse environmental effects of coal mining and burning, specially in power stations including: Generation of hundreds of millions of tons of waste products, including fly ash, bottom ash, flue gas desulfurization sludge, that contain mercury, uranium, thorium, arsenic, and other heavy metals . Besides Acid rain from high sulfur coal, Interference with groundwater and water table levels, Contamination of land and waterways and destruction of homes from fly ash spills such as Kingston Fossil Plant coal fly ash slurry spill , Impact of water use on flows of rivers and consequential impact on other land-uses , Dust nuisance and Subsidence above tunnels, sometimes damaging infrastructure.



For example, coal-fired power plants without effective fly ash capture are one of the largest sources of human-caused background radiation exposure. This is because; Coal-fired power plants emit mercury, selenium, and arsenic which are harmful to human health and the environment. Release of carbon dioxide, a greenhouse gas, which causes climate change and global warming according to the Intergovernmental panel on climate change(IPCC) and the United States Environmental Protection Agency(USEPA).

As it is indicated by various literatures; Coal is the largest contributor to the human-made increase of CO₂ in the air. Potential environmental and health effects of coal include:

- Effluent discharges to water can affect water quality and the health of aquatic organisms.
- SO₂ emissions can result in the acidification of lakes, rivers and soil, and can have severe respiratory effects in humans.
- Metal emissions from smelters include human carcinogens, and can also affect terrestrial and aquatic ecosystems and etc

1.2 Petroleum; *Its Origin, Classification and Mining*

Dear student, in the previous content, you have introduced the origin of coal, its ranking and processing, now you learn about the origin, classification and mining of Petroleum. From your previous knowledge, can you mention the origin of petroleum? Let warm up your self with the following activities.

	Learning task 1.2	
a) Define petroleum and list the most common forms of petroleum		
b) Mention some of the main origin and classification of petroleum		
c) State the mining process of petroleum		

1.2.1 Petroleum: *overview*

Petroleum or **crude oil** is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of various molecular weights hydrocarbons and other organic compounds. The term *petroleum* comes from the Latin stems *petra*, “rock,” and *oleum*, “oil.” to describe a broad range of hydrocarbons found in gas, liquid, or solid forms beneath the earth surface.

Petroleum is found in many parts of the world which include the Middle East, southern United States, Mexico, Nigeria, the former Soviet Union and recently it is found in other countries of the world. Crude oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish). In the reservoir it is usually found in association with **natural gas**, which being lighter forms a gas cap over the petroleum, and **saline water** which, being heavier than most forms of crude oil, generally sinks beneath it. Crude oil may also be found in semi-solid form mixed with sand and water, where it is usually referred to as **crude bitumen**.

Dear student, can you explain the difference between natural gas and crude oil?

1.2.2 Origin of Petroleum

Dear student, the origin of petroleum is based on Biogenic theory and Abiogenic theory. These theories can be elaborated as follows: Can you explain the difference between Biogenic and Abiogenic.

i) Biogenic theory

Most geologists view crude oil, like coal and natural gas, as the product of compression and heating of ancient vegetation over geological time scales. According to this theory, it is formed from the decayed remains of prehistoric marine animals and terrestrial plants. Over many centuries this organic matter, mixed with mud, is buried under thick sedimentary layers of material.

ii) Abiogenic theory

In 1866, Berthelot proposed that carbides formed by the action of alkali metal on carbonates react with water to give rise to large quantities of acetylene, which can in turn be converted in to petroleum at elevated temperatures and pressures.

1.2.3 Mining of petroleum

Dear student, mining of petroleum is not a simple task; it needs the knowledge of various disciplines. Can you explain why it is not simple task?

The vast majority of petroleum is found in oilfields or reservoirs below the earth's surface. The oil is sometimes under high pressure and can flow to the surface on its own without pumping. However, most wells require induced pressure using water, carbon dioxide, natural gas or steam in order to bring the oil to the surface.

1.2.4 Composition and classification of Petroleum

Dear student, from your previous knowledge, can you mention some of the composition of petroleum. Generally, knowing the chemistry of petroleum is important because it can help to know its physical and chemical properties.

Petroleum is principally a mixture of a very large number of hydrocarbons; such as alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, and heavier hydrocarbons and this

bituminous material is usually referred to as bitumen or asphalt along with trace amount of various nitrogenous and sulfurous compounds, nickel, vanadium and other elements. The overall tank Composition of Petroleum is listed in table 1.1 below.

Table 1.1 Composition of Petroleum

Element	Percentage composition
Carbon	83.0-87.0
Hydrogen	10.0-14.0
Nitrogen	0.1-2.0
Sulfur	0.05-6.0
Oxygen	0.05-1.5
Nickel and Vanadium	Trace levels (\approx 1000 ppm).



Petroleum industries generally classify crude oils by their:

- Geographic location of production
- API gravity (oil's industry measure of density) and
- Sulfur content.

For example, crude oil may be considered light if it has low density or heavy if it has high density; and It may be referred to as sweet if it contains relatively little sulfur or sour if it contains substantial amounts of sulfur. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

1.2.5 Petroleum refining (Distillation of Petroleum) and Processing

Dear student, in the previous content, you have learnt the origin, classification and mining of petroleum. Now you learn about distillation of petroleum (petroleum refining). Can you mention how petroleum is distilled? Let warm up your self with the following activities.

	Learning task 1.2.5	
<p>a) What are the common process units' distillations of petroleum?</p> <p>b) List the major steps/processes in petroleum refining</p> <p>c) What are the major products during distillation of crude oil?</p>		

Raw oil or unprocessed crude oil is not very useful in the form it comes in out of the ground. Therefore, it needs to be broken down into parts and refined before use in a solid material such as plastics and foams or as petroleum fossil fuels as in the case of automobile and air plane engines. An oil refinery is an industrial process plant where crude oil is separated into different hydrocarbon fractions by distillation to produce Ethane and other short-chain alkanes which are used as fuel, Liquid petroleum gas (LPG), naphtha, gasoline (petrol), jet fuel, kerosene, diesel oil, lubrication oils, fuel oils and other hydrocarbons. Each fraction is a complex mixture. For example, more than 500 different hydrocarbons can be found in the gasoline fraction. The common process units in an oil refinery and Schematic of the distillation of crude oil are listed in figure 1.2.5 and table 1.2.5 below.

Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. Later the development of the internal combustion engine led to the production of gasoline and diesel fuels. The evolution of the airplane created an initial need for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry. Common petroleum products include gasoline, liquefied refinery gas, still gases, kerosene, aviation fuel, distillate fuel oil, residual fuel oil, lubricating oils, asphalt, coke and petrochemical feed stocks.

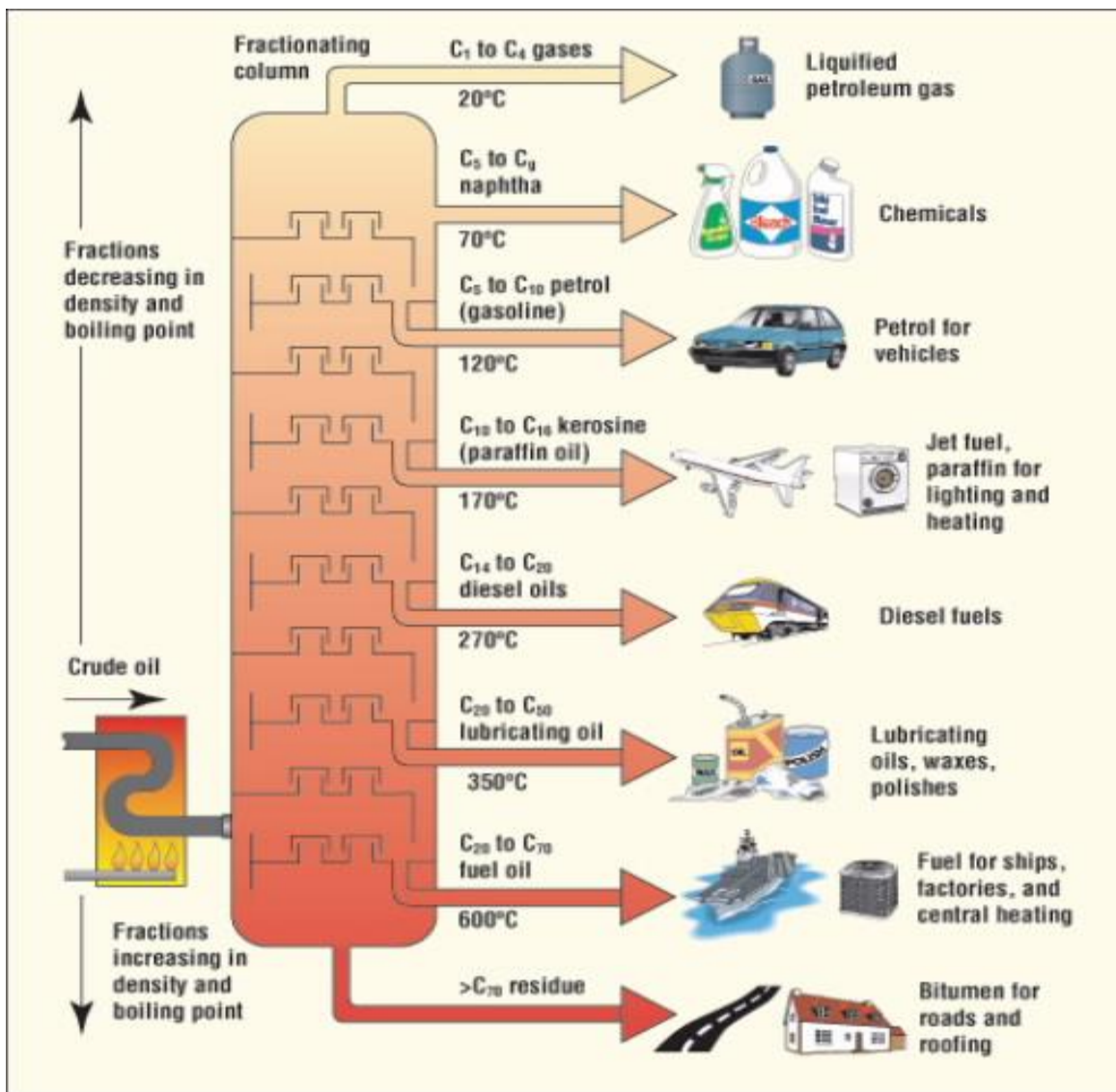


Figure 1.2.5 Schematic of the distillation of crude oil

Dear student, under this main content you learn about the use of Cracking, Alkylation, Hydro treating and Reforming in oil refining. Do you know the terms before? Let warm up your self with the following activities

Learning task 1.2.5.1
<p>a) Define Cracking, Alkylation, Hydro treating and Reforming in terms of oil refining</p> <p>b) What is the difference among Cracking, Alkylation, Hydro treating and reforming in oil refining?</p>

Dear student; *Cracking, Hydrocracking, Hydro treating, Catalytic Reforming and Steam Cracking* are common process units in petroleum refinery processes.

i) Cracking

In an oil refinery cracking processes, allow the production of light products (such as LPG and gasoline) from heavier crude oil distillation fractions (such as gas oils) and residues. Fluid Catalytic Cracking (FCC) produces a high yield of gasoline and LPG while Hydrocracking is a major source of jet fuel, gasoline components and LPG. Thermal cracking is currently used to upgrade very heavy fractions or to produce light fractions or distillates, burner fuel and/or petroleum coke.

Two extremes of the thermal cracking in terms of product range are represented by the high-temperature process called steam cracking or pyrolysis (750-900 °C or more) which produces valuable ethylene and other feed stocks for the petrochemical industry, and the milder-temperature delayed coking (500°C) which can produce, under the right conditions, valuable needle coke, a highly crystalline petroleum coke used in the production of electrodes for the steel and aluminum industries.

ii) Hydrocracking

Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen. The products of this process are saturated hydrocarbons; depending on the reaction conditions (temperature, pressure, and catalyst activity) these products range from ethane, LPG to heavier hydrocarbons comprising mostly of isoparaffins. Hydrocracking is normally facilitated by a bifunctional catalyst that is an Introduction to Energy Sources capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes.

Major products from hydrocracking are jet fuel, diesel, relatively high octane rating gasoline fractions and LPG. All these products have a very low content of sulfur and contaminants. Alkylation is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as a alkyl carbocation, a free radical or a carbanion. In a standard oil refinery process, alkylation involves low-molecular-weight olefins (primarily a mixture of propylene and

butylenes) with isobutene in the presence of a catalyst, either sulfuric acid or hydrofluoric acid. The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffin hydrocarbons. Alkylate is a premium gasoline blending stock because it has exceptional antiknock properties and is clean burning.

Most crude oils contain only 10 to 40 percent of their hydrocarbon constituents in the gasoline range, so refineries use cracking processes, which convert high molecular weight hydrocarbons into smaller and more volatile compounds. Polymerization converts small gaseous olefins into liquid gasoline-size hydrocarbons. Alkylation processes transform small olefin and iso-paraffin molecules into larger iso-paraffins with a high octane number. Combining cracking, polymerization, and alkylation can result in a gasoline yield representing 70 percent of the starting crude oil.

iii) Hydro treating

Hydro treating is a process where a petroleum fraction is reacted with hydrogen for the purpose of removing impurities. The process is usually used to remove sulfur. Hydro treating processes use hydrogen from the catalytic reformer or a hydrogen plant.

Table 1.2.5 Common Process Units in an Oil Refinery

Unit process	Function
Atmospheric Distillation Unit	Distills crude oil into fractions
Vacuum Distillation Unit	Further distills residual bottoms after atmospheric distillation
Hydro-treater Unit	Desulfurizes naphtha from atmospheric distillation, before sending to a Catalytic Reformer Unit
Catalytic Reformer Unit	Reformats paraffins to aromatics, olefins, and cyclic hydrocarbons, which are having high octane number
Fluid Catalytic Cracking	Break down heavier fractions into lighter, more valuable products – by means of catalytic system
Hydro-cracker Unit	Break down heavier fractions into lighter, more valuable products – by means of steam

Alkylation Unit	Produces high octane component by increasing branching or alkyl
Dimerization Unit	Smaller olefinic molecules of less octane number are converted to molecules of higher octane number by dimerization of the smaller olefins
Isomerization Unit	Straight chain normal alkanes of less octane number are isomerized to branched chain alkane of higher octane number

iv) Catalytic Reforming



Catalytic reforming is used to improve the quality of naphtha from the crude distillation unit. The catalytic reforming unit uses a *catalyst* to allow the chemical reactions to take place under "reasonable" temperatures and pressure and "encourage" the desired hydrocarbons to be produced.

v) Steam Cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (commonly olefins), including ethane (ethylene) and propene (propylene).

1.2.6 Gasoline/petrol and Diesel: *Production, composition, properties and rating*

Dear student, in the previous content, you have learnt how a petroleum is refined. Now you learn Production, composition, properties and rating of petrol and Diesel. From your experience, can you compare the rate of petrol and Diesel? Let warm up your self with the following activities

	Learning task 1.2.6	
<p>a) Compare and contrast the rate of petrol and diesel in our country</p> <p>b) What is octane rating?</p>		

1.2.6.1 Production of Petrol vs Diesel

Petroleum is refined to produce petrol and diesel. Fractional Distillation process is used for refining of petroleum. At various temperatures; different byproducts are formed from it. Petrol and diesel both are derived at varying temperatures during refining process. Petrol is produced at

temperature between 35 degrees to 200 degrees while diesel is produced at a boiling point of 250-350 degrees. After distillation, in order to use these byproducts as commercially acceptable petrol and diesel, some blending with other elements has to be done. Petrol is produced first in this process as it is produced at a lower temperature than diesel.

1.2.6.2 Composition and properties of petrol vs diesel

Diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approx. $C_{10}H_{20}$ to $C_{15}H_{28}$. Petrol consists of hydrocarbons with between 5 and 12 carbon atoms per molecule but then it is blended for various uses. Overall a typical petrol sample is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), aromatics and olefins (alkenes). The ratios vary on a variety of factors. Petrol is more volatile than diesel, not only because of the base constituents, but because of the additives that are put into it. Gasoline contains about 34.6 megajoules per litre (MJ/l) while diesel contains about 38.6 megajoules per litre. This gives a higher power to diesel.

1.2.6.3 Rating of petrol vs diesel

Octane number is a figure of merit representing the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal combustion engine. Such detonation is wasteful of the energy in the fuel and potentially damaging to the engine; premature detonation is indicated by knocking or ringing noises that occur as the engine operates. The octane number of a sample of fuel is determined by burning the gasoline in an engine under controlled conditions,

Example, of spark timing, compression, engine speed, and load, until a standard level of knock occurs. The engine is next operated on a fuel blended from a form of isooctane (octane number 100) that is very resistant to knocking and a form of heptane (octane number 0) that knocks very easily. When a blend is found that duplicates the knocking intensity of the sample under test, the percentage of isooctane by volume in the blended sample is taken as the octane number of the fuel. Octane numbers higher than 100 are determined by measuring the amount of tetraethyl lead that must be added to pure isooctane so as to duplicate the knocking of a sample fuel. Factors

which can increase the octane number are more branching: 2-methylbutane is less likely to auto ignite than pentane. Shorter chains: pentane is less likely to auto ignite than heptane.

Dear student, Petrol and diesel are petroleum-derived liquid mixtures used as fuels. Though both have similar base product but have different properties and usage.

1.2.7 Uses of petroleum

Dear student, can you mention some of the uses of petroleum; it has various uses.

Most of the crude oil is used in the production of fuels such as gasoline, kerosene, and fuel oil. Non-fuel uses include petroleum solvents, industrial greases and waxes, or as raw materials for the synthesis of *petrochemicals*. Petroleum products are used to produce synthetic fibres such as nylon and other polymers such as polystyrene, polyethylene and synthetic rubber. They also serve as raw materials in the production of pharmaceuticals, fertilizers, refrigerants, aerosols, antifreeze, detergents, dyes, adhesives, alcohols, explosives and pesticides. The H_2 given off in refinery operations can be used to produce a number of inorganic petrochemicals, such as ammonia, ammonium nitrate, and nitric acid from which most fertilizers as well as other agricultural chemicals are made.



Chapter Summary



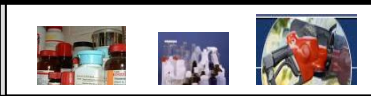
- Coal and Petroleum Processing is an industrial process that can be used for the manufacturing of coal and petroleum in the desired quality
- **Coal** is a readily combustible black or brownish-black sedimentary rock normally occurring in rock strata in *layers or veins* called **coal beds**
- There are different types of Coal the major ones are peat, lignite, Bituminous coal, Steam coal or Anthracite , Sub-bituminous coal and graphite,
- **Carbonization** is defined as “The destructive distillation of organic substances in the absence of air accompanied by the production of carbon and liquid and gaseous products”.
- **Coal gasification** can be used to produce syngas, a mixture of carbon monoxide (CO) and hydrogen (H₂) gas.
- Hydrogenation of coal is direct conversion of coal to liquids. For example, one of the main methods of direct conversion of coal to liquids by hydrogenation process is the Bergius process
- **Petroleum** is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds. The two most common forms are *natural gas and crude oil*.
- Petroleum is a combination of gaseous, liquid and solid mixtures of many alkanes. It consists principally of a mixture of hydrocarbons, with traces of various nitrogenous and sulfurous compounds.
- An oil refinery is an industrial process plant where crude oil is processed in three ways in order to be useful petroleum products.
- Cracking, Alkylation, Hydro treating and Reforming are processes in petroleum refining which can be used for distillation or refining petroleum in to different desired products



Self test exercises





1. A coal has different ranking; explain for the base of ranking
2. Explain the three different factors for coal formation
3. Mr. X and Mr. Y bought the same mass of coal and charcoal respectively. Their objective is to test which one has highest amount of energy. According to your opinion which will give highest amount of energy through burning? Justify your answer
4. Discuss briefly the difference among carbonization, gasification and hydrogenation of coal
5. Explain why, mining of petroleum is not a simple task
6. Some of the Common Process Units in an Oil Refinery are Atmospheric Distillation Unit and Vacuum Distillation Unit; explain the difference between the two processes
7. Explain briefly the major products during distillation of crude oil
8. Discuss briefly how Cracking, Alkylation, Hydro treating and Reforming are used in petroleum refining
9. When we rate diesel and petrol some of the parameters are octane number and chemical composition:
 - a) Define octane number
 - b) Compare and contrast Chemical composition of petrol and diesel
10. From what you have read about crude oil and natural, what is the composition of
 - (i) Crude oil
 - (ii) Commercial natural gas
 - (iii) LPG?

 Chapter 2	Main Petrochemicals	
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Unit Introduction

Dear student, this chapter deals with introduction to petrochemicals. We will also discuss further about Chemical conversions for manufacture of petrochemicals, how Petrochemicals are manufactured from Methane, Ethylene, Propylene, Butylenes and BTX and Manufacture of Acetylene, Ethylene oxide, Acrylonitile, Dimethylterephthalate

	Learning objective of the unit	
<p>Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:</p> <ul style="list-style-type: none"> • Define petrochemicals • Discuss what type of chemical conversions are applied for manufacture of petrochemicals • Explain how petrochemicals are manufactured from Methane, Ethylene, Propylene, Butylenes and BTX • Explain how Acetylene, Ethylene oxide, Acrylonitile, Dimethyl terephthalate are manufactured from different raw materials 		

2.1. Introduction to petrochemicals

Dear student, under this main content you learn about what petrochemicals are. Let warm up your self with the following activities.

	Learning task 2.1	
<ul style="list-style-type: none"> a) Define petrochemicals b) Explain how different chemicals are manufactured from petrochemicals c) Explain the major use of petrochemicals 		

Petrochemicals are non-fuel chemical compounds derived from petroleum. These chemicals include a large number of organic compounds (aliphatic and aromatic) of various functional groups. Examples include benzene and its derivatives, methane, ethylene, propylene, butene, toluene, and xylene and their derivatives. Some compounds are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.

The birth of petrochemicals has been one of the wonderful stories connected with modern chemical and chemical engineering research. The basic raw materials supplied by the petroleum refineries or the natural-gas companies are LPG, or liquid petroleum gases, natural gases, gas from cracking processes, liquid distillate from C₄-C₉, and distillates from special cracking processes, as well as cyclic fractions for aromatics.

2.2. Chemical conversions for manufacture of petrochemicals

Dear student, under this sub content you learn what type of chemical conversions are essential for the manufacture of petrochemicals.

The production of the hundreds of commercially produced petrochemicals is based largely on efficient and, in many cases, novel chemical processing, developed by the research and development of the various companies. For these chemical processes the basis is the chemical reaction, or the chemical conversion. Chemical engineers directing the chemical processing in the present highly competitive chemical economy have called upon many branches of basic science, engineering, and management to improve their manufacturing in all phases, supplementing, but including, many former procedures.

The conversion of refinery feedstock into final products entails three main stages. The first stage is the manufacture of the *base chemicals or the building blocks* (e.g. *ethylene, propylene, benzene*). They are next converted into *intermediate products* (e.g. *ethanol, ethylene glycol, propylene glycol, styrene, etc.*). In the third stage, these intermediate products are then either further processed or converted into products that are used directly by industry to produce finished consumer products (e.g. polyethylene, polypropylene, polystyrene, polyvinylchloride).

The oil and gas industry involvement in petrochemicals is primarily in these three stages, that is, the manufacture of base chemicals all the way through to their subsequent conversion into plastics resins (polyethylene and polypropylene).

The "**Base Chemicals**" can be broadly classified into two groups: **olefins and aromatics**. Olefins are characterized by chains of carbon atoms as their backbone while aromatics contain a ring of carbon atoms at the core of the molecule. In an olefin plant, the long chained carbon molecules are cracked (split) into smaller chains, such as C₂ (ethylene), C₃ (propylene) and C₄ (butadienes). The two cracking methods used are thermal cracking (high temperature) and catalytic cracking (in the presence of a catalyst), both of which are highly energy intensive.

2.3. Petrochemicals from Methanol, Ethylene, Propylene, Butylenes and BTX

Dear student, under this sub content you learn how Petrochemicals are manufactured from Methanol, Ethylene, Propylene, Butylenes and BTX.

As it is discussed before, the two petrochemical classes are olefins including *ethylene and propylene, and aromatics including benzene, toluene and xylene isomers(BTX)*. Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions. Chemical plants produce olefins by steam cracking of natural gas liquids like ethane and propane. Aromatics are produced by catalytic reforming of naphtha. Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents, and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels.

2.3.1 Primary petrochemicals

Primary petrochemicals are divided into three groups depending on their chemical structure:

- Olefins include ethylene, propylene, and butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products similarly, Butadiene is used in making synthetic rubber.
- Aromatics include benzene, toluene, and xylenes(BTX). Benzene is a raw material for dyes and synthetic detergents. Manufacturers use xylenes to produce plastics and synthetic fibers.
- Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate.

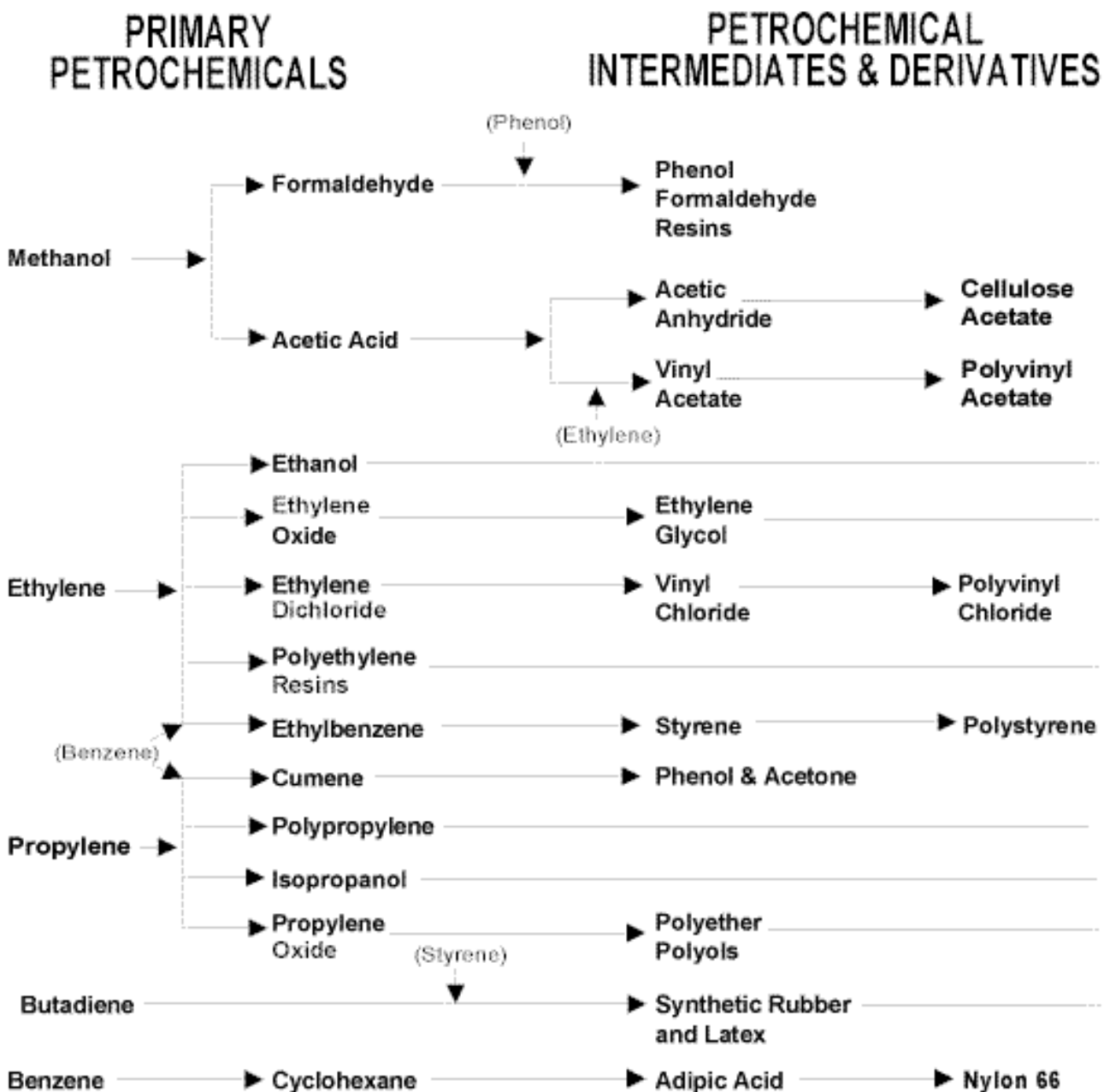


Figure 2.1 Conversion of Primary petrochemicals in to Intermediates and Derivatives petrochemicals

2.3.2 Petrochemical Intermediates and Derivatives

Petrochemical intermediates are generally produced by chemical conversion of primary petrochemicals to form more complicated derivative products. Petrochemical derivative products can be made in a variety of ways; the main ones are:

- Directly from primary petrochemicals;
- Through intermediate products which still contain only carbon and hydrogen; and, through intermediates which incorporate chlorine, nitrogen or oxygen in the finished derivative.
- In some cases, they are finished products; in others, more steps are needed to arrive at the desired composition.

Of all the processes used, one of the most important is **polymerization**. It is used in the production of plastics, fibers and synthetic rubber, the main finished petrochemical derivatives.

Some typical petrochemical intermediates are:

- Vinyl acetate used for paint, paper and textile coatings
- Vinyl chloride used for polyvinyl chloride (PVC)
- Formaldehyde used for Resin manufacture
- Ethylene glycol used for polyester textile fibers
- Styrene which is important in rubber and plastic manufacturing.

Dear student, the following are some major chemicals that are produced from ethylene, Propylene benzene, toluene and xylene. Can you mention some of the chemicals that can be produced from these chemicals?

2.3.3 Chemicals produced from methanol

Methanol is the simplest alcohol. Various types of chemicals are produced from methanol. For example:

- Formaldehyde-via methanol oxidation
- Acetic acid-via oxidation of formaldehyde
- Phenol formaldehyde- via addition of phenol on formaldehyde
- Acetic anhydride- via addition of ethylene on acetic acid and finally it produce cellulose acetate

PETROCHEMICAL INTERMEDIATES & DERIVATIVES

MAJOR END USE MARKETS

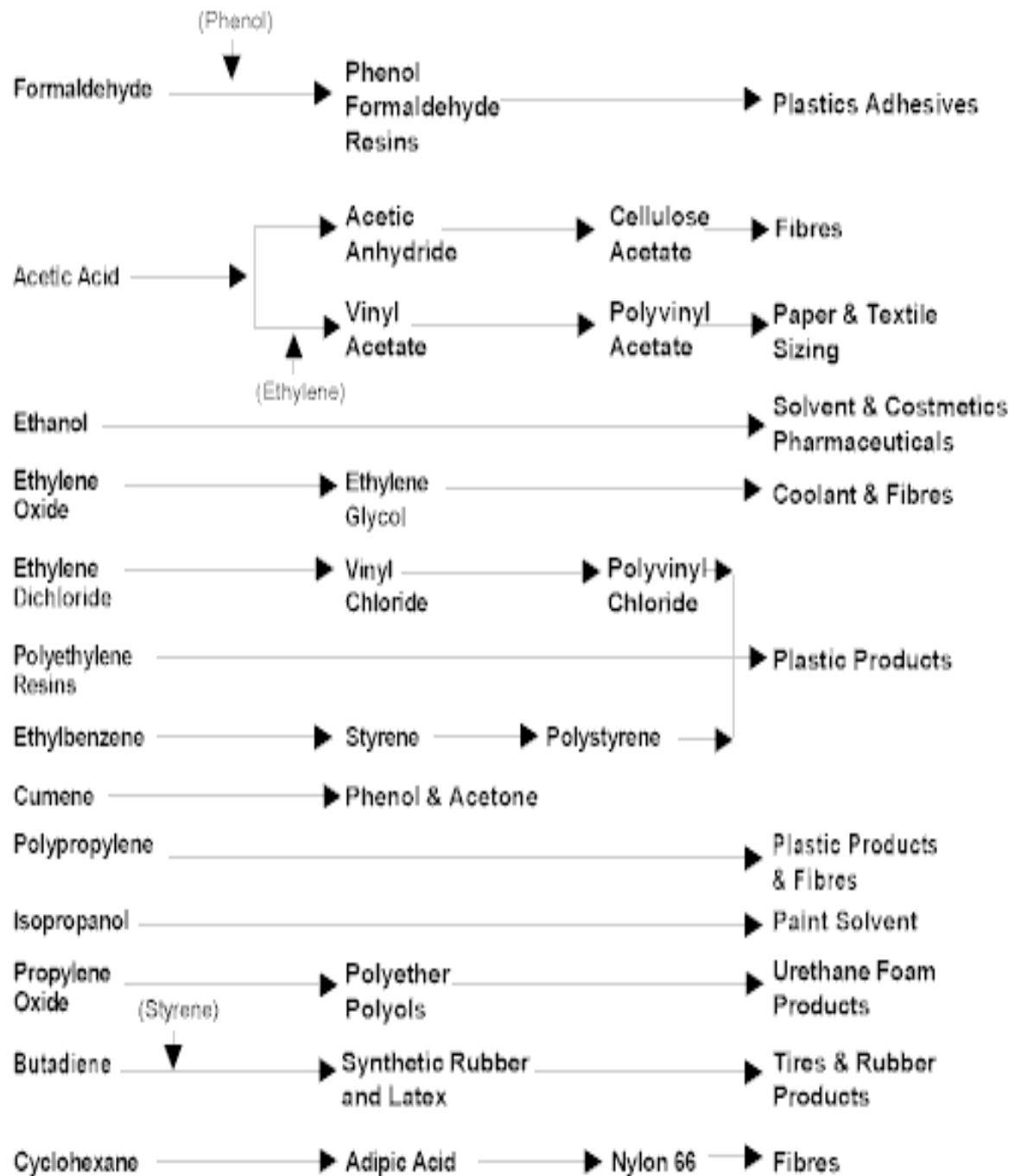


Figure 2.2 Conversion of Intermediates and Derivatives petrochemicals in to major end use

2.3.4 Chemicals produced from ethylene

Ethylene is the simplest olefin which is used as a chemical feedstock and ripening hormone, Some of these compounds synthesized include:-

- Polyethylene-by polymerization of ethylene
- Ethanol - via ethylene hydration of ethylene
- Ethylene oxide - via ethylene oxidation
- Ethylene glycol (engine coolant)- via ethylene oxide hydration
- Polyesters - any of several polymers with ester linkages in the backbone chain
- Glycol ethers - via glycol condensation
- Ethoxylates , vinyl acetate , 1,2-dichloroethane , trichloroethylene
- Tetrachloroethylene (or perchloroethylene)- used as a dry cleaning solvent and degreaser
- Vinyl chloride- monomer for polyvinyl chloride (PVC) - plastic used for piping, tubing, other things

2.3.5 Chemicals produced from propylene and their uses

Propylene is used as a monomer and a chemical feedstock

- Isopropyl alcohol (or 2-propanol)- often used as a solvent or rubbing alcohol
- Polypropylene - polymerized propylene
- Propylene oxide - used in engine coolant and aircraft deicer fluid
 - ✓ polyol - used in the production of polyurethanes
 - ✓ glycol ethers - from condensation of glycols
- Acrylic acid
 - ✓ acrylic polymers
 - ✓ allyl chloride
 - ✓ epichlorohydrin - chloro-oxirane; used in epoxy resin formation
- Epoxy resins - polymerizing glue from bisphenol A, epichlorohydrin, and some amine
- C₄ hydrocarbons - a mixture consisting of butanes, butylenes and butadienes
 - ✓ isomers of butylene - useful as monomers or co-monomers
 - ✓ isobutylene - feed for making methyl *tert*-butyl ether (MTBE) or monomer for copolymerization with a low percentage of isoprene to make butyl rubber

- 1,3-butadiene (or buta-1,3-diene) - a diene often used as a monomer or co-monomer for polymerization to elastomers such as polybutadiene, styrene-butadiene rubber, or a plastic such as acrylonitrile-butadiene-styrene (ABS)
- Synthetic rubbers - synthetic elastomers made of any one or more of several petrochemical (usually) monomers such as 1,3-butadiene, styrene, isobutylene, isoprene, chloroprene; elastomeric polymers are often made with a high percentage of conjugated diene monomers such as 1,3-butadiene, isoprene, or chloroprene
- Higher olefins
 - ✓ polyolefins such poly-alpha-olefins which are used as lubricants
 - ✓ alpha-olefins - used as monomers, co-monomers, and other chemical precursors. For example, a small amount of 1-hexene can be copolymerized with ethylene into a more flexible form of polyethylene.
 - ✓ other higher olefins
 - ✓ detergent alcohols

2.3.6 Chemicals produced from benzene and their uses

Dear student, the following are some major chemicals that are produced from benzene.

Benzene is the simplest aromatic hydrocarbon. Various chemicals can be prepared from benzene. The main are the following.

- Ethylbenzene - made from benzene and ethylene
- Styrene- made by dehydrogenation of ethylbenzene; used as a monomer of polystyrene
- Cumene - isopropylbenzene; a feedstock in the cumene process
- Phenol - hydroxybenzene; often made by the cumene process
- Acetone - dimethyl ketone; also often made by the cumene process
- Bisphenol A - a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate
 - ✓ epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine
 - ✓ polycarbonate - a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)
- Solvents - liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes

- Cyclohexane - sometimes used as a non-polar solvent. Adipic acid - a 6-carbon dicarboxylic acid which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon. nylons - types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines. caprolactam - a 6-carbon cyclic amide. Nylons are types of polyamides, some are from polymerizing caprolactam .Nitrobenzene - can be made by single nitration of benzene. aniline - aminobenzene
- Methylene diphenyl diisocyanate (MDI) - used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas ,polyurethanes
- alkylbenzene - a general type of aromatic hydrocarbon which can be used as a precursor for a sulfonate surfactant (detergent). Detergents are often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates , chlorobenzene

2.3.7 Chemicals produced from toluene

Toluene or methylbenzene can be a solvent or precursor for other chemicals such as:

- Benzene
- Toluene diisocyanate (TDI) - used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
 - Polyurethanes - a polymer formed from diisocyanates and diols or polyols
- Benzoic acid - carboxybenzene ; caprolactam ; nylon

2.3.8 Chemicals produced from xylenes

Mixed xylenes - any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals.

ortho-xylene - both methyl groups can be oxidized to form (*ortho*-)phthalic acid phthalic anhydride

para-xylene - both methyl groups can be oxidized to form terephthalic acid

- Dimethyl terephthalate - can be copolymerized to form certain polyesters
- Polyesters - although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.
- Terephthalic acid - often copolymerized to form polyethylene terephthalate ;polyesters

meta-xylene e.g isophthalic acid used as alkyd resins ,Polyamide Resins and Unsaturated Polyesters

2.4. Manufacture of Acetylene, Ethylene oxide, Acrylonitrile, Dimethyl terephthalate

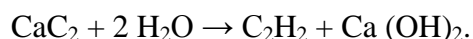
Dear student, under this sub content you learn how Acetylene, Ethylene oxide, Acrylonitrile, Dimethyl terephthalate are industrially manufactured

2.4.1 Manufacture of Acetylene (C₂H₂)

Dear student, in your practical organic chemistry I, you have manufactured acetylene from calcium carbide and water. Besides, there are other methods that can be used for the preparation of acetylene. Acetylene is a colorless, combustible gas with a distinctive odor.

2.4.1.1 Manufactory process

Commercial purposes, acetylene can be made from several different raw materials depending on the process used. One simplest process involves reaction of calcium carbide with water to produce acetylene gas and calcium carbonate slurry, called hydrated lime. The chemical reaction may be written as:



This reaction produces a considerable amount of heat, which must be removed to prevent the acetylene gas from exploding. There are several variations of this process in which either calcium carbide is added to water or water is added to calcium carbide. Both of these variations are called wet processes because an excess amount of water is used to absorb the heat of the reaction. A third variation, called a dry process, uses only a limited amount of water, which then evaporates as it absorbs the heat.

Other processes use natural gas, which is mostly methane, or a petroleum-based hydrocarbon such as crude oil, or naphtha, as raw materials; Coal can also be used. These processes use high temperature (thermal cracking process) to convert the raw materials into a wide variety of gases,

including hydrogen, carbon monoxide, carbon dioxide, acetylene, and others. The chemical reaction for converting methane into acetylene and hydrogen may be written:



2.4.1.2 Storage and handling of Acetylene

When acetylene is liquefied, compressed, heated, or mixed with air, it becomes highly explosive. As a result special precautions are required during its production and handling. , it must be stored and handled with great care. When it is transported through pipelines, the pressure is kept very low and the length of the pipeline is very short.

2.4.1.3 Uses of Acetylene

The most common use of acetylene is as a raw material for the production of various organic chemicals including 1,4-butanediol, which is widely used in the preparation of polyurethane and polyester plastics. The second most common use is as the fuel component in oxy-acetylene welding and metal cutting. Some commercially useful acetylene compounds include acetylene black, which is used in certain dry-cell batteries, and acetylenic alcohols, which are used in the synthesis of vitamins.

2.4.2 Manufacture of Ethylene oxide (C₂H₄O)

Dear student, do you know how ethylene oxide, is manufactured, warm up your self what will be the manufacturing process ethylene oxide.

2.4.1.1 Manufactory of Ethylene oxide: Ethylene oxide is a flammable, colorless gas. At temperatures above 51.3 °F it smells like ether at toxic levels. Ethylene oxide is found in the production of solvents, antifreeze, textiles, detergents, adhesives, polyurethane foam, and pharmaceuticals. It is also useful in fumigants, sterilants for spices and cosmetics, as well as during hospital sterilization of surgical equipment. In industry ethylene oxide is produced while ethylene and oxygen reacting on a silver catalyst at 200–300 °C and pressures used are in the region of 1-2MPa. $\text{CH}_2=\text{CH}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$

The typical yield for this reaction is 70-80%, the major side reaction being combustion of ethylene to produce carbon dioxide. Many other methods are proposed to produce ethylene oxide but no other methods are accepted by industry.

2.4.2.2 Chemical reactivity of Ethylene Oxide

The Ethylene oxide is highly reactive chemical and can react specially in the presence of a catalyst with compounds such as water, alcohols, ammonia, amines, and organic acids. These reactions can be self-accelerating and generate considerable quantities of heat. Therefore, it is most important to ensure inadvertent mixing with other chemicals, including water does not occur. It is the reactivity of ethylene oxide which makes it as important as the feedstock for the preparation of other useful chemicals. Ethylene oxide itself is used as a disinfectant, sterilizing agent in controlled circumstances.

2.4.2.3 Uses of ethylene oxide

The chemical compound ethylene oxide is an important industrial chemical used as an intermediate in the production of ethylene glycol, other chemicals, and sterile for the manufacturing of rubber, paint, leather processing, Industrial Surfactants, Paper, Textile, Metal processing, Latex & Waxes, Household surfactants, Detergents, Pharmaceutical raw materials, Dyeing & finishing, Agrochemicals, Cosmetics raw material. Ethylene oxide is also used in other industries where heat-sensitive goods are sterilized and in the manufacture of choline chloride, glycol ethers and polyglycols. Other minor uses world-wide include its application in the manufacture of rocket propellant and petroleum demulsifiers.

2.4.3 Manufacture of Acrylonitrile (C₃H₃N)

Acrylonitrile, vinyl cyanide, CH₂=CHC≡N, is a colorless liquid with a slightly pungent odor. It was first prepared in 1893 by a French Chemist, Ch. Moreau, by dehydration of ethylene cyanohydrin with phosphorus pentoxide. It is an important monomer for the manufacture of useful plastics. Of all the nitriles, Acrylonitrile is manufactured on probably the largest scale. Most industrial acrylonitrile is produced by catalytic ammoxidation of propylene by the Sohio

process in the presence of a metal-oxide catalyst. Small amounts of water is fed to the reactor to increase the selectivity of acrylonitrile and decrease the temperature within the reactor

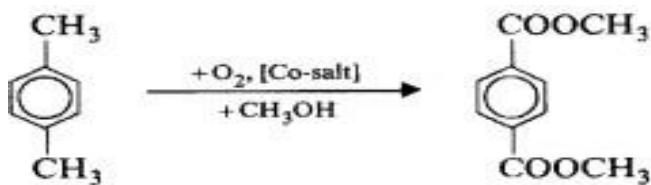


2.4.3.1 Health effects of Acrylonitrile

Acrylonitrile is highly flammable and toxic. It undergoes explosive polymerization. The burning acrylic materials release toxic fumes of hydrogen cyanide and oxides of nitrogen. Exposure to acrylonitrile can then occur from emissions, auto exhaust, and cigarette smoke through inhalation, oral, and occasional dermal routes. Acrylonitrile increases cancer in high dose .

2.4.4 Manufacture of Dimethyl terephthalate (DMT)

The most important commercial route to ester and acid manufacture is the liquid-phase oxidation of p-xylene. However, if no special precautions are taken, the oxidation stops at p-toluic acid: The crude esters are separated into their components in a system of columns under vacuum. The p-toluic acid ester is recycled to the oxidation. The dimethyl terephthalate is further purified by recrystallizing twice from methanol or xylene, melted, and converted into readily manageable flakes with a drum flaker. The dimethyl terephthalate selectivity is about 85 % (based on p-xylene) and roughly 80% (based on CH₃OH).



Manufacture of dimethyl terephthalate from p-xylene

The crude dimethyl terephthalate selectivity is said to be greater than 90% (based on p-xylene) and 60-70% (based on methanol). DMT is used in the manufacture of polyester fibre, yarn and film and also certain polyester resins.



Chapter Summary



- Petrochemicals are chemicals, other than fuels, derived from petroleum. These chemicals include a large number of aliphatic and aromatic organic compounds of various functional groups
- The conversion of refinery feedstock into final products entails three main stages: the manufacture of the *base chemicals or the building blocks intermediate products and* intermediate products are then either further processed or converted into products
- Petrochemicals can be manufactured from Methanol, Ethylene, Propylene, Butylenes and BTX(benzene, toluene, Xylene)
- Acetylene, Ethylene oxide, Acrylonitrile, Dimethyl terephthalate are organic compounds that can be manufactured industrially by using different raw materials and different manufacturing process



Self test exercises



1. Chemical conversions for manufacture of petrochemicals needs base chemicals, intermediates and finished products; explain what are base chemicals, intermediates and finished products
2. Compare and contrast Primary petrochemicals and Petrochemical Intermediates and derivatives
3. Explain how Acetylene, Ethylene oxide, Acrylonitrile, Dimethyl terephthalate manufactured industrially
4. Discuss briefly the uses of petrochemicals; support your answer with real situation



Unit Introduction

Dear student, this chapter deals with Basic Organic Products. We will also discuss further: How Organic chemicals are synthesized Industrially, Manufacture of Methanol and Isopropanol, Manufacture of Formaldehyde and Acetaldehyde, Manufacture of Acetic acid, Manufacture of Acetone, Manufacture of Phenol and Styrene



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define Basic Organic Products
- List the main raw materials for manufacturing of different basic organic products
- Explain how different basic organic products are manufactured industrially
- Compare and contrast manufacture of formaldehyde and acetaldehyde
- Compare and contrast manufacture of phenol and styrene
- Mention the main uses of Basic Organic Products

3.1. Introduction to Industrial organic synthesis

Dear student, different organic chemicals are synthesized industrially using different techniques. Do you know how Industrial organic compounds are synthesized, warm up your self with the following activities?



Learning task 3.1



- a) Discuss how Industrial organic synthesis is developed

The Development of Organic Synthesis

The well - being of modern society is unimaginable without the myriad products of industrial organic synthesis. The history of organic synthesis is generally traced back to Wöhler's synthesis of the natural product urea from ammonium isocyanate in 1828. This laid to rest the vital force theory, which maintained that a substance produced by a living organism could not be produced synthetically. The discovery had monumental significance, because it showed that, in principle, all organic compounds are amenable to synthesis in the laboratory.

Organic synthesis is a major facilitator for the chemical industry and a significant contributor to society, applications being found in the pharmaceuticals, fine chemicals, agrochemicals, specialty chemicals, electronics and other related industries

3.2 Manufacture of Methanol and Isopropanol

Dear student, in the previous content you have learnt how Industrial organic compounds is developed. Now, you learn how Methanol and Isopropanol are manufactured, warm up your self with the following activities.



Learning task 3.2



- Mention the main raw materials that are used for manufacture of methanol and isopropanol
- Explain how methanol and Isopropanol are manufactured industrially
- List the major uses of methanol and isopropanol

3.2.1 Industrial Preparation of Methanol

Methanol is a common industrial chemical that has been used as an alternative blended liquid transportation fuel and under consideration for wider use. In many countries, notably in Asia, methanol is almost exclusively used to produce the intermediate chemical formaldehyde as input to urea formaldehyde composite wood adhesive. On industrial scale methanol is prepared from a mixture of carbon monoxide and hydrogen. The gaseous mixture is subjected to 200 atmospheres and then passed over heated catalyst mixture of ZnO and Cr₂O₃ kept at 400^o C to 450^o C. This reaction results the formation of methanol vapors which are then condensed to liquid state.



3.2.2 Manufacture of Isopropanol

Isopropyl alcohol/propan-2-ol/2-propanol (C₃H₈O) (also known as rubbing alcohol) is a colorless, flammable chemical compound with a strong odor. It is the simplest example of a *secondary alcohol*. Isopropyl alcohol is produced by combining water and propene through two processes as shown in the reaction below via.



i) **Indirect hydration:** Here propene reacts with sulfuric acid to form a mixture of sulfate esters. Subsequent hydrolysis of these esters produces isopropyl alcohol. These processes give predominantly isopropyl alcohol rather than 1-propanol because the addition of water or sulfuric acid to propene follows Markovnikov's rule.

ii) **Direct hydration:** Involve reaction of propene with water, either in gas or liquid phases, at high pressures in the presence of solid or supported acidic catalysts.

Uses of Isopropyl alcohol

Isopropyl alcohol is readily available. It is used as antifreeze, rubbing alcohol, solvent and making acetone, soap, antiseptic solutions. Like acetone, it dissolves a wide range of non-polar compounds such as oils, gums, alkaloids, resins. It also evaporates quickly and is *relatively* non-toxic, compared to alternative solvents. Unlike ethanol or methanol, isopropyl alcohol can be separated from aqueous solutions by adding a salt such as sodium chloride, sodium sulfate, or any of several other inorganic salts, since the alcohol is much less soluble in saline solutions than in salt-free water. The process is colloquially called salting out, and causes concentrated isopropyl alcohol to separate into a distinct layer. However, Isopropyl alcohol vapor is denser than air and is highly flammable with a very wide combustible range. Therefore, it should be kept away from heat and open flame.

3.3. Manufacture of Formaldehyde and Acetaldehyde

Dear student, in the previous content you have learnt how Methanol and Isopropanol are manufactured now you learn how Formaldehyde and Acetaldehyde are manufactured. Do you know how Formaldehyde and Acetaldehyde are synthesized, warm up your self with the following activities.



Learning task 3.3



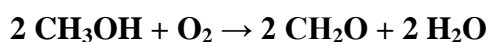
- Explain how Formaldehyde and Acetaldehyde are manufactured industrially
- Mention the main raw materials that are used for manufacture of Formaldehyde and Acetaldehyde
- List the major uses of Formaldehyde and Acetaldehyde

3.3.1 Manufacture of Formaldehyde

Formaldehyde (methanal) is the simplest aldehyde with the formula CH_2O .

3.3.1.2 Synthesis and industrial production of Formaldehyde

Formaldehyde was first reported by the Russian chemist Aleksandr Butlerov (1828–86) and was conclusively identified by August Wilhelm von Hofmann. Formaldehyde is produced industrially by the catalytic oxidation of methanol. The most common catalysts are silver metal or a mixture of an iron and molybdenum or vanadium oxides. In the more commonly used FORMOX process methanol and oxygen react at ca. 250–400 °C in presence of iron oxide in combination with molybdenum and/or vanadium to produce formaldehyde according to the chemical equation:



Formaldehyde can also naturally occur in the environment where carbon, hydrogen and oxygen exist by the action of sunlight and it becomes part of smog. Natural processes in the upper atmosphere may contribute up to 90 percent of the total formaldehyde in the environment. Formaldehyde is also formed as an intermediate in the oxidation (or combustion) of methane and other carbon compounds, e.g. forest fires, in automobile exhaust, and in tobacco smoke.

3.3.1.3 Applications of Formaldehyde

Dear student Formaldehyde is a common building block for the synthesis of more complex compounds and materials as a result it has various applications.

It is an important precursor to many other chemical compounds, especially for polymers. In approximate order of decreasing consumption, products generated from formaldehyde include urea formaldehyde resin, melamine resin, phenol formaldehyde resin, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate.

The textile industry uses formaldehyde-based resins as finishers to make fabrics crease-resistant. Formaldehyde-based materials are key to the manufacture of automobiles, and used to make components for the transmission, electrical system, engine block, door panels, axles and brake shoes. Aqueous solutions of formaldehyde are referred to as **formalin**. "100%" formalin consists of a saturated solution of formaldehyde (this is about 40% by volume or 37% by mass) in water, with a small amount of stabilizer, usually methanol to limit oxidation and degree of polymerization. Formalin is used as disinfectant and preservation of organic specimens in biological system.

Typical commercial grade formalin may contain 10–12% methanol in addition to various metallic impurities. The diol also exists in equilibrium with a series of short polymers (called oligomers), depending on the concentration and temperature. In view of its widespread use, toxicity and volatility, exposure to formaldehyde is a significant consideration for human health.

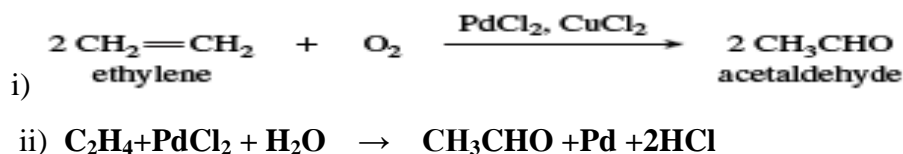
3.3.2 Manufacture of Acetaldehyde

Acetaldehyde (CH₃CHO), also called ethanal, is an aldehyde used as a starting material in the synthesis of 1-butanol (*n*-butyl alcohol), ethyl acetate, perfumes, flavorings, aniline dyes, plastics, synthetic rubber, and other chemical compounds. Pure acetaldehyde is a colorless.

Dear student, there are various manufacturing methods of Acetaldehyde; the main ones are the following:

3.3.2.1 Manufacture of Acetaldehyde by Oxidation of Ethylene

Wacker – Chemie and Farbwerke Hoechst, developed the direct liquid phase oxidation of ethylene in 1957 – 1959. The catalyst is an aqueous solution of PdCl₂ and CuCl₂. In 1894, F.C. Phillips observed the reaction of ethylene with an aqueous palladium chloride solution to form acetaldehyde.



3.3.2. 2 Manufacture of Acetaldehyde from Ethyl Alcohol:

Acetaldehyde is produced commercially by the catalytic oxidation of ethyl alcohol. Passing alcohol vapors and preheated air over a silver catalyst at 480⁰C carries out the oxidation.



Acetaldehyde also, produced commercially by the dehydrogenation of ethyl alcohol.

Reaction: $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2$; Catalyst: Cu -Co-Cr₂O₃ Temperature: 280– 350⁰ C.

3.3.2.3 Manufacture of Acetaldehyde from Acetylene:

Acetaldehyde has been produced commercially by the hydration of acetylene since 1916. However, the development of the process for the direct oxidation of ethylene in the 1960s has almost completely replaced the acetylene– based processes and in 1976 there was only small volume production in a few European countries. In the older processes, acetylene of high purity is passed under a pressure of 103.4 kPa (15 psi) into a vertical reactor containing a mercury catalyst dissolved in 18-25% sulfuric acid at 70-90⁰C.



3.4. Manufacture of Acetic acid

Dear student, in the previous content you have learnt how Formaldehyde and Acetaldehyde are manufactured; now you learn how Acetic acid is manufactured. Do you know how acetic acid is manufactured? Warm up your self with the following activities.



Learning task 3.4



- Mention the main raw materials that are used for manufacture of Acetic acid
- Explain how Acetic acid is manufactured industrially
- List the major uses of Acetic acid

3.4.1 Properties of acetic acid

Acetic acid (CH_3COOH) is a colorless liquid that has a distinctive sour taste and pungent smell. Although it is classified as a weak acid, acetic acid is highly dangerous to skin. Acetic acid is one of the simplest carboxylic acids. It is an important chemical reagent and industrial chemical, mainly used in the production of cellulose acetate mainly for photographic film and polyvinyl acetate for wood glue, as well as synthetic fibers and fabrics. In households, diluted acetic acid is often used in descaling agents.

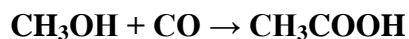
In the food industry, acetic acid is used under the food additive as a condiment. Dilute acetic acid produced by natural fermentation is called vinegar. Acetic acid is produced industrially both synthetically and by bacterial fermentation.

3.4.2 Manufacture of acetic acid

Dear student, there are various methods for manufacture of acetic acid. The main ones are as follows

3.4.2.1 Manufacture of acetic acid by Methanol carbonylation

Most acetic acid is produced by methanol carbonylation. In this process, methanol and carbon monoxide react to produce acetic acid according to the chemical equation:



The process involves iodomethane as an intermediate, and occurs in three steps. A catalyst, usually a metal complex, is needed for the carbonylation.

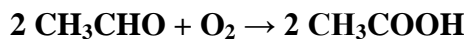
1. $\text{CH}_3\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{I} + \text{H}_2\text{O}$
2. $\text{CH}_3\text{I} + \text{CO} \rightarrow \text{CH}_3\text{COI}$
3. $\text{CH}_3\text{COI} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HI}$

By altering the process conditions, acetic anhydride may also be produced on the same plant

3.4.2.2 Manufacture of acetic acid by Acetaldehyde oxidation



Under similar conditions and using similar catalysts as are used for butane oxidation, the oxygen in air to produce acetic acid can oxidize acetaldehyde.



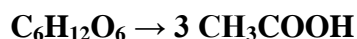
3.4.2.3 Manufacture of acetic acid by Oxidative fermentation

For most of human history, acetic acid bacteria of the genus *Acetobacter* have made acetic acid, in the form of vinegar. Given sufficient oxygen, these bacteria can produce vinegar from a variety of alcoholic foodstuffs. Commonly used feeds include apple cider, wine, and fermented grain, malt, rice, or potato mashes. The overall chemical reaction facilitated by these bacteria is:



3.4.2.4 Manufacture of acetic acid by anaerobic fermentation

Species of anaerobic bacteria, including members of the genus *Clostridium*, can convert sugars to acetic acid directly, without using ethanol as an intermediate. The overall chemical reaction conducted by these bacteria may be represented as:



3.5. Manufacture of Acetone

Dear student, in the previous content you have learnt how Acetic acid is manufactured; now you learn how Acetone is manufactured. Do you know how Acetone is manufactured? Warm up your self with the following activities.



Learning task 3.5



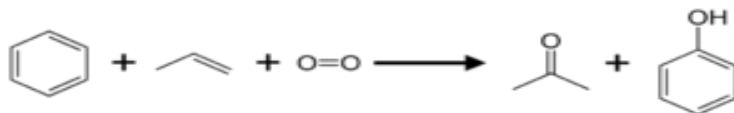
- Mention the main raw materials that are used for manufacture of Acetone
- Explain how Acetone is manufactured industrially
- List the major uses of Acetone

3.5.1 Properties of Acetone

Acetone ($(\text{CH}_3)_2\text{CO}$) is a colorless, flammable liquid miscible with water. It serves as an important solvent and for cleaning purposes in the laboratory. It is a common building block in organic chemistry. Acetone is also naturally produced and disposed of in the human body as a result of normal metabolic processes.

3.5.2 Manufacture of acetone

Cumene process: Benzene is alkylated with propylene and the resulting cumene (isopropylbenzene) is oxidized by air to give phenol and acetone:

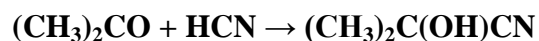


Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone. Besides, Small amounts of acetone are produced in the body by the decarboxylation of ketone bodies. Acetone is a by product of fermentation in the distillery industry.

3.5.3 Uses of acetone

About one third of the world's acetone is used as a solvent. Acetone is a good solvent for most plastics and synthetic fibers including those used in laboratory bottles made of polystyrene, polycarbonate and some types of polypropylene. Acetone is used as a solvent in pharmaceutical industry and as a denaturation agent in denatured alcohol. In the laboratory, acetone is used as a polar aprotic solvent in a variety of organic reactions, such as S_N2 reactions. The use of acetone solvent is also critical for the Jones oxidation. It is a common solvent for rinsing laboratory glassware because of its low cost and volatility; however, it does not form an azeotrope with water.

Acetone is also present as an excipient in some pharmaceutical products. Acetone is present in a variety of general medical and cosmetic applications and is also listed as a component in food additives and food packaging. A quarter of world's acetone produced is consumed as a precursor to methyl methacrylate. This application begins with the initial conversion of acetone to acetone cyanohydrin:



3.5.4 Safety issues

The most common hazard associated with acetone is its extreme flammability. Acetone has been studied extensively and is generally recognized to have low acute and chronic toxicity if ingested and/or inhaled. For example, inhalation of high concentrations (around 9200 ppm) in the air caused irritation of the throat in humans in as little as 5 minutes.

3.5.5 Environmental effects of acetone

Acetone evaporates rapidly, even from water and soil. Once in the atmosphere, it is degraded by UV light with a 22-day half-life. Acetone dissipates slowly in soil, animals, or waterways since it is sometimes consumed by microorganisms, but it is a significant groundwater contaminant due to its high solubility in water.

3.6. Manufacture of Phenol and Styrene

Dear student, in the previous content you have learnt how acetone is manufactured; now you learn how Phenol and Styrene are manufactured. Do you know how Phenol and Styrene are synthesized, warm up your self with the following activities.



Learning task 3.6

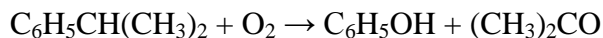


- Mention the main raw materials that are used for manufacture of Phenol and Styrene
- Explain how Phenol and Styrene are manufactured industrially
- List the major uses of Phenol and Styrene

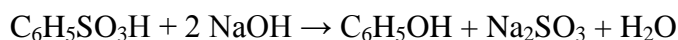
3.6.1. Manufacture of Phenol

Phenol, also known as **carbolic acid**, is an organic compound with the chemical formula C_6H_5OH . It is a white crystalline solid. The molecule consists of a phenyl ($-C_6H_5$), bonded to a hydroxyl ($-OH$) group.

Because of phenol's commercial importance, many methods have been developed for its production. The main route being practiced presently involves the partial oxidation of cumene (isopropylbenzene) via the Hock rearrangement:



The first commercial route begins with the reaction of strong base with benzenesulfonate:



Other methods involve conversions of chlorobenzene, using base or steam (Raschig-Hooker process). It is a recoverable byproduct of coal pyrolysis.

Uses of phenol

The major uses of phenol involve its conversion to plastics or related materials. Condensation with acetone gives bisphenol-A, a key building block for polycarbonates. Condensation with formaldehyde gives phenolic resins, the most famous of which is Bakelite. Hydrogenation of phenol gives cyclohexanone, an intermediate en route to nylon. Nonionic detergents are produced by alkylation of phenol to give the alkylphenols, which are then subjected to ethoxylation.

Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceuticals. Phenol is also used as an oral anesthetic/analgesic, commonly used to temporarily treat pharyngitis. Phenol was widely used as an antiseptic, especially as Carbolice soap, from the early 1900s through the 1970s.

3.6.2 Manufacture of Styrene (vinyl benzene)

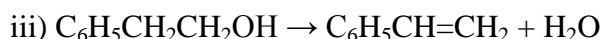
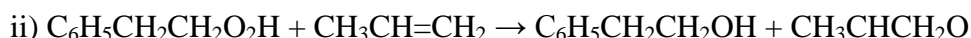
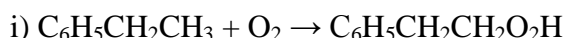
Styrene, also known as **vinyl benzene**, is an organic compound with the chemical formula $C_6H_5CH=CH_2$. This derivative of benzene is a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations confer a less pleasant odor. Styrene is the precursor to polystyrene and several copolymers. Styrene is produced in industrial quantities from ethylbenzene, which is in turn prepared on a large scale by alkylation of benzene with ethylene.

3.6.2.1 Manufacture of Styrene by dehydrogenation of ethyl benzene

Styrene is most commonly produced by the catalytic dehydrogenation of ethyl benzene. Ethylbenzene is mixed in the gas phase with 10–15 times its volume in high-temperature steam, and passed over a solid catalyst bed. Most ethylbenzene dehydrogenation catalysts are based on iron (III) oxide, promoted by several percent potassium oxide or potassium carbonate. Steam serves several roles in this reaction. It is the source of heat for powering the endothermic reaction, and it removes coke that tends to form on the iron oxide catalyst through the water gas shift reaction. $C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH=CH_2 + H_2$

3.6.2.2 Manufacture of Styrene via ethylbenzenehydroperoxide

Commercially styrene is also co-produced with propylene oxide in a process known as POSM (Lyondell Chemical Company) or Shell for styrene monomer/propylene oxide. In this process ethylbenzene is treated with oxygen to form the ethylbenzene hydroperoxide. This hydroperoxide is then used to oxidize propylene to propylene oxide. The resulting 2-phenylethanol is dehydrated to give styrene:



3.6.2.3 Other methods

Styrene can be produced from toluene and methanol, which are cheaper raw materials than those in the conventional process. Historically, however, this process has suffered from low selectivity due to competing decomposition of methanol. Another developing route to styrene is via benzene and ethane.

Health effects of styrene: Styrene is regarded as a "hazardous chemical", especially in case of eye contact, but also in case of skin contact, of ingestion and of inhalation, according to several sources.



Chapter Summary



- Organic synthesis is a major facilitator for the chemical industry and a significant contributor to society, applications being found in the pharmaceuticals, fine chemicals, agrochemicals, specialty chemicals, electronics and other related industries.
- Methanol is a common industrial chemical that has been used as an alternative blended liquid transportation fuel and under consideration for wider use
- Formaldehyde is a naturally occurring substance in the environment made of carbon, hydrogen and oxygen. When produced in the atmosphere by the action of sunlight and oxygen

on atmospheric methane and other hydrocarbons, it becomes part of smog. Aqueous solutions of formaldehyde are referred to as **formalin**.

- Acetic acid is one of the simplest carboxylic acids. It is an important chemical reagent and industrial chemical, mainly used in the production of cellulose acetate mainly for photographic film and polyvinyl acetate for wood glue, as well as synthetic fibres and fabrics
- Acetone is a good solvent for most plastics and synthetic fibers including those used in laboratory bottles made of polystyrene, polycarbonate and some types of polypropylene. Acetone is used as a solvent by the pharmaceutical industry and as a denaturation agent in denatured alcohol.



Self test exercises



1. Industrial organic synthesis is manufacturing process of different organic compounds industrially, some of these are manufacturing of formaldehyde and acetaldehyde; explain the basic manufacturing process of these chemicals
2. Phenol and styrene are some organic compounds that can be produced industrially.
 - a) Mention the main raw materials that are used for manufacture of Phenol and Styrene
 - b) Discuss the main uses of these chemicals
 - c) Explain the health effect and environmental aspect of these chemicals
3. Acetic acid one organic acid that is frequently used in laboratories and industries
 - a) List the common manufacturing process for the acid
 - b) Mention the common uses of acetic acid
 - c) Explain the health effect and environmental aspect of acetic acid
4. Compare and contrast the industrial manufacturing of methanol and isopropanol to that of Laboratory preparation
5. Acetone is the organic compound with the formula $(\text{CH}_3)_2\text{CO}$
 - a) Discuss the industrial manufacture of acetone
 - b) Mention some of the use of it
 - c) Explain the health effect and environmental aspect of acetone



Unit Introduction

Dear student, this chapter deals with Plastics, Rubber and Fibers. We will also discuss further about Nomenclature of polymers, Addition and condensation polymerization, Methods of Polymerization, Properties and classification of plastics, Effect of polymer structure on properties, Properties and classification of rubber, Properties and classification of fibers



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define Plastics, Rubber and Fibers
- Explain how Nomenclature of polymers is performed
- Mention the main Methods of Polymerization
- Compare and contrast Addition and condensation polymerization
- Mention the common properties of plastics
- Mention the major classification of plastics
- Explain how polymer structure affect its properties
- Explain Properties of rubber
- Mention the major classification of rubber
- Explain Properties of rubber
- Mention the major classification of rubber
- Compare and contrast natural fibers and synthetic fibers

4.1. Introduction to polymers

Dear student, under this main content you learn about the polymers. Do you know what polymers are? Let warm up your self with the following activities.



Learning task 4.1



- What are polymers?
- State the difference between monomer and polymer
- Explain the difference between natural polymer and synthetic polymer

The Polymer Industry

4.1.1. Introduction

Dear student, industrial use of polymers started when Goodyear discovered the vulcanization of rubber in 1839. Polymer research rapidly spread throughout the world after 1930 and this led to the development of many synthetic polymers including nylon, polyethylene and polyvinyl chloride. The term polymer comes from two Greek words: “polys” which means “many” and “meros” which means “parts.” A polymer is therefore a high molecular weight compound made up of hundreds or thousands of many identical small basic units (monomers) of carbon, hydrogen, oxygen or silicon atoms. The monomers are linked together covalently in a chemical process known as polymerization.

A **polymer** is a large molecule (macromolecule) composed of repeating structural units. These subunits are typically connected by covalent chemical bonds. Although the term *polymer* is sometimes taken to refer to plastics, it actually encompasses a large class comprising both natural and synthetic materials with a wide variety of properties. Because of the extraordinary range of properties of polymeric materials, they play an essential and ubiquitous role in everyday life. This role ranges from familiar synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life. Polymers are studied in the fields of polymer chemistry, polymer physics, and polymer science.



Figure 4.1.1 The polymerization process

Natural polymeric materials such as shellac, amber, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. The list of synthetic polymers includes synthetic rubber, bakelite, neoprene, nylon, PVC, polystyrene, polyethylene, polypropylene, polyacrylonitrile, PVB, silicone, and many more. **Biopolymers** are one form of polymers which are biological origin. Some of common biopolymers are:

- i) Nucleic acid polymers (DNA, RNA):-which carry genetic information of the cell
- ii) Amino acids polymers (Proteins):- Which have structural and catalytic roles in the cell
- iii) Sugar Polymers (Carbohydrates):-Are source of energy

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene, whose repeating unit is based on ethylene monomer.

4.1.2. Classification of polymers

Dear student, can you mention the major classification of polymers?

Polymers can be classified into three types:

- 1. Linear polymers** in which the repeating units are similar to the links in a very long chain. They are known as polymer chains. An example is polyethylene
- 2. Branched polymers** in which some of the molecules are attached as side chains to the linear chains. The individual molecules are still discrete.
- 3. Three-dimensional cross-linked polymers** in which branched chains are joined together by cross-linking in a process known as “curing”. Vulcanization of rubber is a curing process.

4.2. Nomenclature of polymers

Dear student, in the previous content you have learnt what polymers are and the major types of polymers; now you learn about the Nomenclature of polymers. From your previous background can you explain how Nomenclature of polymers is given? Let warm up your self with the following activities.



Learning task 4.2



- Explain how Nomenclature of polymers is given
- Discuss how classification of polymers is based on Nomenclature of polymers
- Explain the difference between Homochain polymers and Hetrochain polymers

Classification and Nomenclature

One of the classifications of polymers is based on Polymer Structure. For example polymers can be Homochain or Hetrochain polymers.

(1) Homochain polymers

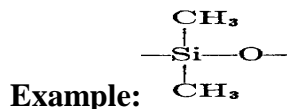
Polymers having all carbon atoms along their backbone are important examples of homochain polymers. They may be further classified depending upon whether there are single, double, or triple bonds along their backbone. Carbon-chain polymers with only single bonds along the backbone $-\text{[C-C -C]}-$ are known as *polyalkylenes* (or polyalkylidenes). These include polystyrene, the polyolefins (e.g., polyethylene and polypropylene), and polyvinyl chloride.

Carbon-chain polymers with double bonds along the chain $-\text{[C=C]}-$ such as the dieneelastomers- polyisoprene and polybutadiene-are called polyalkenylenes.

<u>Polymer</u>	<u>Monomer(s)</u>	<u>Structural repeating unit</u>
Polystyrene	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}$
<i>cis</i> -1,4-Polyisoprene (natural rubber)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$
Poly(vinyl chloride)	$\text{CH}_2=\text{CHCl}$	$-\text{CH}_2-\text{CHCl}-$
Polybutadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$

(2) Heterochain polymers

Heterochain polymers that contain more than one atom type in their backbone are grouped according to the types of atoms and chemical groups (e.g., carbonyl, amide, or ester) located along the backbone. Another important class of heterochain polymers includes polysiloxanes. These have a -Si-O- backbone with methyl or other substituent groups attached to silicon.



As the preceding examples illustrate, a very large number of different polymer structures are possible. In order to identify these as unambiguously as possible, it is important to establish a nomenclature system. As already evident, simple vinyl polymers are designated by attaching the prefix *poly* to the monomer name (e.g., polystyrene, polyethylene, and polypropylene). However, when the monomer name consists of more than one word or is preceded by a letter or number, the monomer is enclosed by parentheses preceded by the prefix *poly*. For example the polymer obtained from the polymerization of vinyl acetate is poly (vinyl acetate).

Nomenclature rules for non-vinyl polymers such as condensation polymers are generally more complicated than for vinyl monomers. These polymers are usually named according to the initial monomer or the functional group of the repeating unit. For example the most important commercial nylon, commonly called nylon-6, 6 (66 or 6/6), is more descriptively called poly(hexamethylene adipamide). Which denote the polyamidation of hexamethylenediamine (alternately called 1, 6-hexane diamine) with adipic acid.

In some cases, the common names are used almost exclusively in place of the more chemically-correct nomenclature. For example, the polycondensation of phosgene and bisphenol-A-the common name for 2,2-bis(4-hydroxyphenyl)propane-produces the engineering thermoplastic, polycarbonate. Often, the prefix bisphenol-A is placed before polycarbonate to distinguish it from other polycarbonates that can be polymerized by using bisphenol monomers other than bisphenol-A, such as tetramethyl bisphenol-A.

For convenience, several societies have developed a very useful set of two-, three-, and four-letter abbreviations for the names of many common thermoplastics, thermosets, fibers,

elastomers, and additives. Sometimes, abbreviations adopted by different societies for the same polymer may vary, but there is widespread agreement on the abbreviations for a large number of important polymers. These abbreviations are convenient and widely used. For example, PS is generally recognized as the abbreviation for polystyrene, PVC for poly(vinyl chloride), PMMA for poly(methyl methacrylate), and PTFE for polytetrafluoroethylene.

4.3. Methods of polymerization

Dear student, in the previous content you have learnt how Nomenclature of polymers is given; now you learn about Methods of polymerization. From your previous background can you explain the major Methods of polymerization? Let warm up your self with the following activities.



Learning task 4.3



- a) Define polymerization
- b) List the common methods of polymerization
- c) Explain the difference between Addition and condensation polymerization

Dear student, in our introduction part of this chapter, you have introduced what are polymers, and therefore, it will be simple for you to define polymerization.

Polymerization reaction is a type of reaction that produces polymers from monomers. Polymerization reaction can be undergoing by various methods. The main ones are ***addition polymerization*** and ***condensation polymerization***.

In addition to classifying polymers on the basis of their processing characteristics, polymers may also be classified according to the mechanism of polymerization. For example, thousands of polymers have been synthesized and more will be produced in the future. Fortunately, all polymers can be assigned to one of two groups based upon their processing characteristics or type of polymerization mechanism. More specific classification can be made on the basis of polymer structure.

4.4. Addition and Condensation polymerization

Dear student, in the previous content you have learnt Methods of polymerization; now you learn about Addition and Condensation polymerization. From your previous background can you explain the difference between Addition and Condensation polymerization? Let warm up your self with the following activities



Learning task 4.4

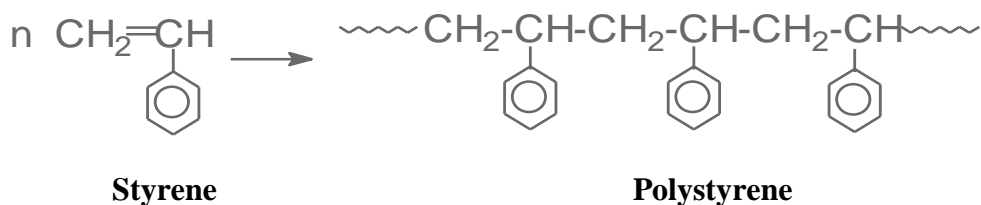


- Define Addition and Condensation polymerization
- Explain the difference between Addition and condensation polymerization
- Give examples of polymers that are formed by Addition and condensation polymerization

4.4. 1 Addition polymerization

Dear student, from your organic chemistry course you have learned that organic compounds that have a double bond or triple bond can undergo addition reaction. Similarly addition polymerization needs a monomer which has a double bond.

Addition polymerization is a polymerization process that is produced by successive addition reactions. A carbon- carbon double bond is needed in the monomer. Most important addition polymers are polymerized from ethylene-based monomers. Polyethylene which is polymerized by a sequential addition of ethylene monomers is an example of most important addition polymers. Free radicals catalyze usually initiate addition polymerization reaction. For this purpose organic peroxides (ROOR) are frequently used. The reaction proceeds in three steps; Free radical formation, propagation of polymer chain and termination of free radical reaction. The polymer is the only product, which involves the opening out of a double bond. Oxygen is often used as the initiator.

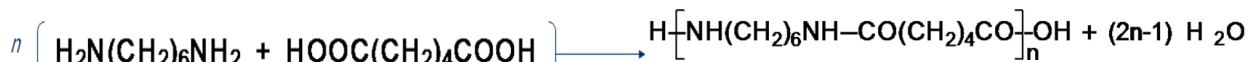


4.4.2 Condensation polymerizations

Dear student, from your organic chemistry you have learned esterification reaction is an example of condensation reaction, in which an alcohol and organic acid are reacted and form an ester and water. Similarly condensation polymers are obtained by the random reaction of two molecules.

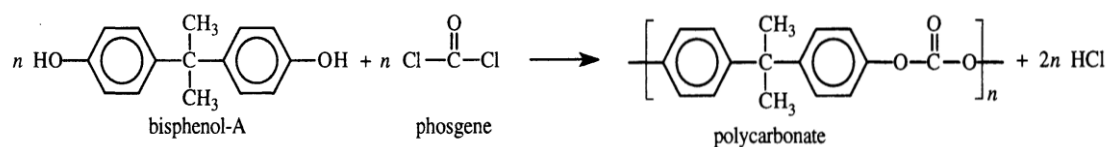
Condensation polymerization occurs between monomer or higher molecular weight intermediate (oligomers) each having complementary functional end units, such as carboxylic acid or hydroxy groups. Typically, condensation polymerizations occur by the liberation of a small molecule in the form of a gas, water, or salt. Common condensation polymers include polyesters (possess ester linkage) and polyamides (possess amide linkage).

Example : Synthesis of nylon-6,6 by condensation of adipic acid and hexamethylene diamine.



The molecular formula of the condensation polymer is not an integral multiple of the formula, of the monomer molecule owing to the elimination of a by-product, which in this case is water. This polymerization is accompanied by the liberation of two molecules of water for each repeating unit. Another important example of a polycondensation is the preparation of polycarbonate from bisphenol-A and phosgene. In this case, two molecules of hydrogen chloride are formed for each repeating unit.

Alternately, if the sodium salt of bisphenol-A was used in the polymerization, the by-product of the condensation would be sodium chloride rather than hydrogen chloride. The salt will precipitate out of the organic solvent used for the polymerization and, therefore, can be easily and safely removed.



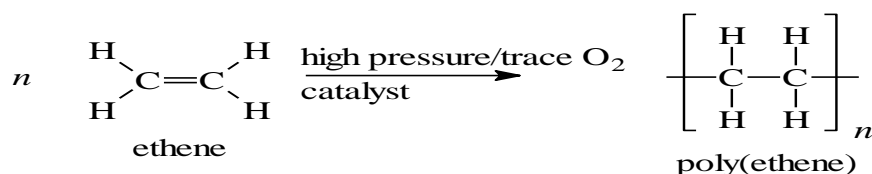
Dear student, Classification of polymerization is mostly based upon Polymerization Mechanism.

More recently, another classification scheme based on polymerization kinetics has been adopted over the more traditional addition and condensation categories. According to this scheme, all polymerization mechanisms are classified as either *step growth* or *chain growth*.

i) **Step growth:** Here high-molecular-weight polymer is formed only near the end of the polymerization (i.e., at high monomer conversion, typically >98%). Most condensation polymers are placed here.

ii) **Chain growth:** Involve subsequent joining of monomers by a reaction involving loss of simple molecule, usually water. Most addition polymers are chain growth. Examples include naturally-occurring synthetic condensation polymers: cellulose, chitin, hair, fur, leather, feathers and nylon (synthetic).

Block copolymer is a polymer molecules of which built from alternating polymeric blocks of two or more different polymers.



4.5 Effect of polymer structure on properties

Dear student, in the previous content you have learnt the difference between Addition and Condensation polymerization; now you learn the Effect of polymer structure on properties. From your previous background can you explain how polymer structure has an effect on its properties?

Let warm up your self with the following activities.



Learning task 4.5



- a) Explain how polymer structure can affect the properties of a polymer
- b) List some of the main properties of polymers

Based on polymer structure, the properties of a given polymer can be varying.

4.5.1 Properties of polymers:

i) Molecular weight: The molecular weight of polymers is not fixed because of varying chain length.

ii) Crystallinity: Because of high molecular weight and varying chain length, most polymers are amorphous and only semi-crystalline. Those with high crystallinity are tougher, more opaque, and more resistant to solvents, higher density and sharply defined melting point. Synthetic polymers may consist of both crystalline and amorphous regions. However, few synthetic polymers are entirely crystalline. The degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.

iii) Glass transition temperature: At low temperature, even amorphous polymers are hard and brittle (glass-like). As temperature is increased, kinetic energy increases. However, motion is restricted to short-range vibrations and rotations as long as glass-like structure is retained. At a certain temperature called the glass transition temperature, a polymer loses glass-like properties. It becomes softer and more elastomeric but it does not melt. If heating is continued further, the polymer will lose elastomeric properties and melt to a flowable liquid.

Dear student, In addition to the above mentioned properties of polymers, polymers have the following typical properties

- Good chemical resistant at room temperature
- Low density, brittleness at low temperature
- Low strength and chemical resistance at high temperature
- Processibility at relatively low temperature
- Generally good insulators(except conductive polymers)
- Often transparent and good optical properties
- Gas permeability
- Recycling

4.6 Plastics-properties and classification

Dear student, in the previous content you have learnt the effect of polymer structure on properties; now you learn properties and classification of plastics. From your previous background can you mention the main properties and classification of plastics? Let warm up your self with the following activities



Learning task 4.6



- a) What are plastics?
- b) List the major properties of plastics
- c) Explain the basic classification of plastics
- d) Compare and contrast thermoplastics and thermosetting
- e) List some of the major uses of plastics

4.6.1 Plastics

Dear student, do you know plastic, what are they? What is their main use to human being?

A plastic is a material that contains as an essential ingredient, an organic substance of a large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow. In practice, a plastic is usually considered to be an amorphous or crystalline polymer which is hard and brittle at ordinary temperatures.

The word plastic is derived from the Greek 'plastikos' meaning 'capable of being shaped or molded', or from 'plastos' meaning 'molded'. It refers to their malleability, or plasticity during manufacture, that allows them to be cast, pressed, or extruded into a variety of shapes-such as films, fibers, plates, tubes, bottles, boxes, and much more. The vast majority of plastics are composed of polymers of carbon and hydrogen alone or with oxygen, nitrogen, chlorine or sulfur in the backbone

4.6.2 Thermoplastics

Also known as thermosoftening plastics are high molecular weight polymers whose chains associate through weak Van der Waals forces, stronger dipole-dipole interactions and hydrogen bonding or even stacking of aromatic rings. Thermoplastic material can be softened and molded on heating. They are elastic and flexible above a certain glass transition temperature. There are dozens of kinds of thermoplastics, with each type varying in crystalline organization and density. Some types that are commonly produced today are polyurethane, polypropylene, polycarbonate, celluloid, nylon and acrylic.

Table 4.6.2. Example of thermoplastic and their uses

Plastic type	uses
Nylon	Silk substitute, making parachutes, vehicle tires, fabrics, footwear, fishnets and carpets
Low-density polyethylene (LDPE)	Packaging films, wire and cable insulation, toys, flexible bottles, houseware
High density polyethylene (HDPE)	Bottles, drums, pipes, films, sheets, wire and cable insulation
Polypropylene (PP)	Automobile and appliances parts, furniture, cordage, carpets, film packaging
Polyvinyl chloride (PVC)	Construction, rigid pipes, flooring, wire and cable insulation, film and sheet
Polystyrene (PS)	Packaging (foam and film), foam, insulation, insulation, appliances, houseware

4.6.3 Thermosetting plastics

A thermosetting material is one which involves considerable crosslinking, so that the finished plastic cannot be made to flow or melt. Thermosetting plastics (thermosets) are polymer materials that cure or are made strong/tough by chemical additives (e.g. addition of epoxides or elements such as sulphur), irradiation (such as electron beam processing), and heating (normally above 200°C).

The curing process transforms these materials into plastic or rubber through a cross linking process. Before curing process, they are usually in liquid form, powder or malleable forms that can be moulded to a final form or used as adhesives. The cross links produce a three dimensional rigid structure of the material with large molecular weight and a high melting point. The three dimensional network of bonds in thermosets generally makes them much stronger than thermoplastics. This makes them suitable for high temperature applications up to the decomposition temperature of the material. A thermoset material cannot be melted and reshaped after curing and therefore cannot be recycled unlike thermoplastics. Examples of thermosets include: polyester resin, vulcanized rubber, bakelite and epoxy resin.

Uses of thermosetting plastics

Phenol-formaldehyde (PF):- Electrical and electronic equipment, automobile parts, utensils, handles, plywood adhesives, particle board binder

Urea-formaldehyde (UF):- Similar to PF, textile treatment, coating

Unsaturated polyester (UP):- Construction, automobile parts, marine accessories Epoxy Protective coating, adhesives, electrical and electronics, industrial flooring, material composites

Melamine-formaldehyde (MF). Decorative panels, counter and table tops, dinnerware, in fabrication of plastic objects, additives such as colourants, fillers, plasticizers, lubricants and stabilizers

Table 4.1. Structures and properties of thermoplastics and thermosets

Parameters	Thermoplastics	Thermosetting
Microstructure	-Linear or branch molecules. -No chemical bonds among the molecules	-Cross-linking network with chemical bonds among molecules after the chemical reaction.
Reaction to Heat	-Can be re-softened (physical phase change).	-Cannot be re-softened after cross-linking without degradation
General Properties	-Higher impact strength. -Easier processing. -Better adaptability to complex designs	-Greater mechanical strength. -Greater dimensional stability. -Better heat and moisture resistance
Molecular weight	-Range from 20,000 to 500,000 amu	-Infinite molecular weight

4.7 Molding constituents of plastics in to articles

Dear student, in the previous content you have learnt the properties and classification of plastics; now you learn how molding constituents of plastics can be used for different types of articles. From your previous background can you mention the main properties and classification of plastics? Let warm up your self with the following activities



Learning task 4.7



- a) What is molding?
- b) Explain the use of molding constituents of plastics
- c) Discuss the process of molding of plastics in to articles

Molding of a plastic is a process of making a hollow form or matrix into which a plastic material is placed and which imparts to the material its final shape as a finished article. The common molding of plastics into articles is **blow molding**.

Blow molding also known as **blow forming** is a manufacturing process by which hollow plastic parts are formed. In general, there are three main types of blow molding: extrusion blow molding, injection blow molding, and stretch blow molding. The blow molding process begins with melting down the plastic and forming it into a parison or preform. The parison is a tube-like piece of plastic with a hole in one end in which compressed air can pass through. There are different types of molding. The main ones are the following:

4.7.1 Extrusion blow molding

In extrusion blow molding (EBM), plastic is melted and extruded into a hollow tube (a parison). This parison is then captured by closing it into a cooled metal mold. Air is then blown into the parison, inflating it into the shape of the hollow bottle, container or part. After the plastic has cooled sufficiently, the mold is opened and the part is ejected.

4.7.2 Injection blow molding

The process of **injection blow molding** (IBM) is used for the production of hollow glass and plastic objects in large quantities. In the IBM process, the polymer is injection molded onto a core pin; then the core pin is rotated to a blow molding station to be inflated and cooled. This is the least-used of the three blow molding processes, and is typically used to make small medical and single serve bottles.

4.7.3 Stretch blow molding (SBM)

Here the plastic is first molded into a "preform" using the injection molding process. These preforms are produced with the necks of the bottles, including threads (the "finish") on one end. These preforms are packaged, and fed later (after cooling) into a reheat stretch blow molding machine. The stretching of some polymers, such as PET (polyethylene terephthalate) results in strain hardening of the resin, allowing the bottles to resist deforming under the pressures formed by carbonated beverages. The main applications are bottles, jars and other containers. Blow molding has an advantage of low tool and die cost; fast production rates; ability to mold complex part; produces recyclable parts. But it is limited to hollow parts, wall thickness is hard to control.

4.8 Preparation, properties & uses of PE, PVC and Bakelite

Dear student, in the previous content you have learnt how molding constituents of plastics can be used for different types of articles; now you learn about Preparation, properties & uses of PE, PVC and Bakelite. Let warm up your self with the following activities.



Learning task 4.8



- a) Explain how PE, PVC and Bakelite are prepared?
- b) Mention the major properties of PE, PVC and Bakelite
- c) List uses of PE, PVC and Bakelite

Dear student, since the invention of the first artificial polymer, **bakelite**, the family has quickly grown with the invention of others. Common synthetic organic polymers are polyethylene (polythene), polypropylene, nylon, teflon (PTFE), polystyrene, polyesters, polymethylmethacrylate (called perspex and plexiglas), and polyvinylchloride (PVC).

4.8.1 Preparation, properties & uses of Polyethylene (PE)

4.8.1.1. Introduction

There are three major classes of polyethylene. These are low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Pellets of these plastics are extruded and blown to produce film. This film is used for packaging and making plastic bags. Ethylene is derived from either modifying natural gas (a methane, ethane, propane mix) or from the catalytic cracking of crude oil.

In a highly purified form, it is piped directly from the refinery to a separate polymerization plant. Here, under the right conditions of temperature, pressure and catalysis, the double bond of the ethylene monomer opens up and many monomers link up to form polyethylene. In commercial polyethylene, the number of monomer repeats units' ranges from 1000 to 10,000. Molecular weight ranges from 28,000 to 280,000.

4.8.1.2. The Polyethylene Manufacturing Process

Today, polyethylene manufacturing processes are usually categorized into “high pressure” and “low pressure” operations. The former is generally recognized as producing conventional low density polyethylene (LDPE) while the latter makes high density (HDPE) and linear low density (LLDPE) polyethylenes.

Polyethylene was first produced by the high pressure process by ICI, Britain, in the 1930's. They discovered that ethylene gas could be converted into a white solid by heating it at very high pressures in the presence of minute quantities of oxygen: Ethylene + 10 ppm oxygen 1000 - 3000 bar polyethylene₈₀ - 300°C.

The polymerization reaction which occurs is a random one, producing a wide distribution of molecule sizes. By controlling the reaction conditions, it is possible to select the average molecule size (or molecule weight) and the distribution of sizes around this average (molecular weight distribution). The chains are highly branched (at intervals of 20-50 carbons). ICI named their new plastic “polythene” and found that they were able to produce it in a density range of about 0.915 to 0.930g cm³. It is known today as LDPE and has its single biggest usage in blown film.

The most common method used in industry is to polymerize ethylene by means of a fluidized reactor bed. A fluidized reactor bed consists of metallic catalyst particles that are 'fluidized' by the flow of ethylene gas. This means that the catalyst particles are suspended in the ethylene fluid as ethylene gas is pumped from the bottom of the reactor bed to the top. Before the late 1970's an organic peroxide catalyst was employed to initiate polymerization. However, because the organic peroxide catalyst is not as active as the metallic catalyst, pressures in excess of 100 times the pressure required with metallic catalysts were necessary. Before ethylene is sent to the fluidized bed, it must first be compressed and heated.

4.8.2 Preparation, properties & uses polystyrene (PS) and Polyvinyl Chloride (PVC)

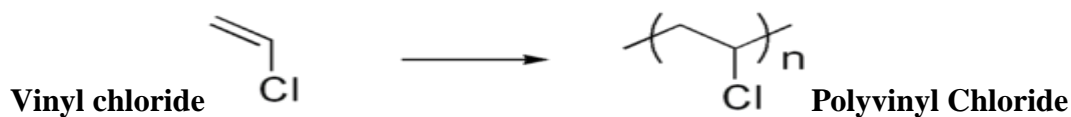
After the First World War, improvements in chemical technology led to an explosion in new forms of plastics. Among the earliest examples in the wave of new plastics were polystyrene (PS) and polyvinyl chloride (PVC).

4.8.2.1 Preparation, properties & uses polystyrene (PS)

Polystyrene is a rigid, brittle, inexpensive plastic that has been used to make plastic model kits and similar knick-knacks. It would also be the basis for one of the most popular "foamed" plastics, under the name *styrene foam* or *Styrofoam*. Foam plastics can be synthesized in an "open cell" form, in which the foam bubbles are interconnected, as in an absorbent sponge, and "closed cell", in which all the bubbles are distinct, like tiny balloons, as in gas-filled foam insulation and flotation devices. In the late 1950s, *high impact* styrene was introduced, which was not brittle. It finds much current use as the substance of toy figurines and novelties.

4.8.2.2 Preparation, properties & uses of Polyvinyl Chloride (PVC)

Polyvinyl Chloride (PVC, commonly called "vinyl") has side chains incorporating chlorine atoms, which form strong bonds. PVC in its normal form is stiff, strong, heat and weather resistant, and is now used for making plumbing, gutters, house siding, enclosures for computers and other electronics gear. PVC can also be softened with chemical processing, and in this form it is now used for shrink-wrap, food packaging, and rain gear.



All PVC polymers are degraded by heat and light. When this happens, hydrogen chloride is released into the atmosphere and oxidation of the compound occurs. Because hydrogen chloride readily combines with water vapor in the air to form hydrochloric acid, polyvinyl chloride is not recommended for long-term archival storage of silver, photographic film or paper.

4.8.3 Preparation, properties & uses of Bakelite

Bakelite is a thermosetting phenol formaldehyde resin, formed from an elimination reaction of phenol with formaldehyde, usually with wood flour filler. It was developed in 1907-1909 by Belgian chemist Dr. Leo Baekeland. It was used for its electrically nonconductive and heat resistant insulators, and also in such products as kitchenware, jewellery, children's toys & etc. Baekeland was looking for an insulating shellac to coat wires in electric motors and generators.

Baekeland found that mixtures of phenol (C_6H_5OH) and formaldehyde ($HCOH$) formed a sticky mass when mixed together and heated, and the mass became extremely hard if allowed to cool. He continued his investigations and found that the material could be mixed with wood flour, asbestos, or slate dust to create "composite" materials with different properties. Most of these compositions were strong and fire resistant. The only problem was that the material tended to foam during synthesis, and the resulting product was of unacceptable quality.

Baekeland built pressure vessels to force out the bubbles and provide a smooth, uniform product. He publicly announced his discovery in 1912, naming it bakelite. It was originally used for electrical and mechanical parts, finally coming into widespread use in consumer goods in the 1920s. Bakelite was the first true plastic. It was a purely synthetic material, not based on any material or even molecule found in nature. It was also the first thermosetting plastic. Conventional thermoplastics can be molded and then melted again, but thermoset plastics form bonds between polymers strands when cured, creating a tangled matrix that cannot be undone without destroying the plastic. Thermoset plastics are tough and temperature resistant.

Bakelite was cheap, strong, and durable. It was molded into thousands of forms, such as cases for radios, telephones and clocks, and balls. Phenol-based ("Phenolic") plastics have been largely replaced by cheaper and less brittle plastics, but they are still used in applications requiring their insulating and heat-resistant properties. For example, some electronic circuit boards are made of sheets of paper or cloth impregnated with phenolic resin.

4.9 Rubber and its properties

Dear student, in the previous content you have learnt Preparation, properties & uses of PE, PVC and Bakelite now you learn about Rubber and its properties. Can you mention some of the properties of rubber? Let warm up your self with the following activities.



Learning task 4.9



- a) Define rubber?
- b) List the major types of rubber
- c) Explain Chemistry and Properties of rubber

4.9.1 Chemistry and Properties of rubber

All rubberlike materials are polymers, which are high molecular weight compounds consisting of long chains of one or more types of molecules, such as monomers. Vulcanization (or curing) produces chemical links between the loosely coiled polymeric chains; elasticity occurs because the chains can be stretched and the crosslinks cause them to spring back when the stress is released.

Natural rubber is a polyterpene, i.e., it consists of isoprene molecules linked into loosely twisted chains. The monomer units along the backbone of the carbon chains are in a *cis* arrangement and it is this spatial configuration that gives rubber its highly elastic character. In gutta-percha, which is another natural polyterpene, the isoprene molecules are bonded in a *trans* configuration leading to a crystalline solid at room temperature. Unvulcanized rubber is soluble in a number of hydrocarbons, including benzene, toluene, gasoline, and lubricating oils.

Rubber is water repellent and resistant to alkalies and weak acids. Rubber's elasticity, toughness, impermeability, adhesiveness, and electrical resistance make it useful as an adhesive, a coating composition, a fiber, a molding compound, and an electrical insulator

4.10 Natural and synthetic rubber

Dear student, in the previous content you have learnt Rubber and its properties now you learn about Natural and synthetic Rubber. Can you explain the difference between Natural and synthetic rubber? Let warm up your self with the following activities.



Learning task 4.10



- a) List the major types of rubber
- b) Explain how synthetic rubber is manufactured
- c) Give examples of natural rubber and artificial rubber

4.10.1 Natural Rubber

Natural rubber is an elastomer (an elastic hydrocarbon polymer) that was originally derived from *latex*, a milky colloidal suspension found in the sap of some plants. It is useful directly in this form (indeed, the first appearance of rubber in Europe is cloth waterproofed with unvulcanized latex from Brazil) but, later, in 1839, Charles Goodyear invented vulcanized rubber; this a form of natural rubber heated with, mostly, sulfur forming cross-links between polymer chains (vulcanization), improving elasticity and durability. The advantages of natural rubber are less buildup of heat from flexing and greater resistance to tearing when hot.

4.10.2 Synthetic rubber

Synthetic rubber is any type of artificially made polymer material, which acts as an elastomer. An elastomer is a material with the mechanical (or material) property that it can undergo much more elastic deformation under stress, than most materials and still return to its previous size without permanent deformation. **Example:** Bromo Isobutylene Isoprene, Polybutadiene. In general, synthetic rubber has the following advantages over natural rubber: better aging and weathering, more resistance to oil, solvents, oxygen, ozone, and certain chemicals, and resilience over a wider temperature range.

The first fully synthetic rubber was synthesized by Sergei Lebedev in 1910. In World War II, supply blockades of natural rubber from South East Asia caused a boom in development of synthetic rubber, notably styrene-butadiene rubber. For example in 1941, annual production of synthetic rubber in the U.S. was only 231 tonnes which increased to 840,000 tonnes in 1945.

4.10.2.1. Styrene Butadiene Rubber (SBR)

Emulsion polymerized styrene-butadiene rubber (E-SBR) is one of the most widely used polymers in the world today. Emulsion SBR is employed in many demanding applications, which enhance the quality of life and contribute significantly to our economy and standards of living. In the 1930's, the first emulsion polymerized SBR known as Buna S was prepared by I. G. Farbenindustrie in Germany. SBR is widely used for rubber belting, hose, flooring, molded goods, rubber soles, coated fabrics etc. It is compatible with natural rubber and has equal performance for automobile tyres. But it is inferior to natural rubber for heavy duty truck tyres.

4.10.2.2. Manufacturing Process

SBR is produced by the copolymerization of butadiene with styrene in the approximate proportion of 3:1 by weight. In the emulsion process, which produces general purpose grades, the feedstocks are suspended in a large proportion of water in the presence of an initiator or a catalyst and a stabiliser. A continuous process is employed. In the solution process, the copolymerisation proceeds in a hydrocarbon solution in the presence of an organometallic complex. This can be either a continuous or batch process.

The emulsion polymerization process has several advantages. It is normally used under mild reaction conditions that are tolerant to water and requires only the absence of oxygen. The process is relatively robust to impurities and amenable to using a range of monomers. Additional benefits include the fact that emulsion polymerization gives high solids contents with low reaction viscosity and is a cost-effective process. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization.

4.10.2.3. Elastomers

An elastomer (or rubber) is a word having its origin from two words: “elastic” which means the ability to return to original shape when a force or stress is removed and “mero” which means “parts“ implying many parts or monomers. Therefore, an essential requirement of an elastomer is that it must be elastic i.e. it must stretch rapidly under tension to several times its original length with little loss of energy as heat.

Industrial elastomers have high tensile strength and high modulus of elasticity. They are amorphous polymers with considerable cross-linkages. The covalent cross-linkages make the elastomer to return to its original structure or shape when the stress is removed. Without cross-linkages or with short chains, the applied force would result in a permanent deformation. They are usually thermosets that require vulcanization, but there are some which are thermoplastic.

Elastomers include:

- Nitrile rubber
- Butyl rubber
- Silicone rubber
- Polyurethane rubber
- Polysulphide rubber
- Poly butadiene
- Styrene-butadiene
- Polyisoprene
- Tetrafluoroethylene
- Tetrafluoropropylene

4.10.2.4. Bioplastics; Cellulose-based plastics

Parkes developed a synthetic replacement for ivory which he marketed under the trade name *Parkesine*, and which won a bronze medal at the 1862 World's fair in London. Parkesine was made from cellulose (the major component of plant cell walls) treated with nitric acid as a solvent. The output of the process (commonly known as cellulose nitrate or pyroxilin) could be dissolved in alcohol and hardened into a transparent and elastic material that could be molded when heated. By incorporating pigments into the product, it could be made to resemble ivory.

Bois Durci is a plastic molding material based on cellulose. It was patented in Paris by Lepage in 1855. It is made from finely ground wood flour mixed with a binder, either egg or blood albumen, or gelatine. The wood is probably either ebony or rose wood, which gives a black or brown resin. The mixture is dried and ground into a fine powder. The powder is placed in a steel

mold and compressed in a powerful hydraulic press while being heated by steam. The final product has a highly polished finish imparted by the surface of the steel mold.

4.10.2.5. Biodegradable (compostable) plastics

Research has been done on biodegradable plastics that break down with exposure to sunlight (e.g., ultra-violet radiation), water or dampness, bacteria, enzymes, wind abrasion and some instances rodent pest or insect attack are also included as forms of biodegradation or environmental degradation. It is clear some of these modes of degradation will only work if the plastic is exposed at the surface, while other modes will only be effective if certain conditions exist in landfill or composting systems.

Starch powder has been mixed with plastic as a filler to allow it to degrade more easily, but it still does not lead to complete breakdown of the plastic. Some researchers have actually genetically engineered bacteria that synthesize a completely biodegradable plastic, but this material, such as Biopol, is expensive at present.

4.10.2.5. Toxicity of plastics

Due to their insolubility in water and relative chemical inertness, pure plastics generally have low toxicity in their finished state, and will pass through the digestive system with no ill effect (other than mechanical damage or obstruction). However, plastics often contain a variety of toxic additives. For example, plasticizers like adipates and phthalates are often added to brittle plastics like polyvinyl chloride (PVC) to make them pliable enough for use in food packaging, toys and teething rings, tubing, shower curtains and other items. Traces of these chemicals can leach out of the plastic when it comes into contact with food. The World Health Organization's International Agency for Research on Cancer (IARC) has recognized the chemical used to make PVC, vinyl chloride, as a known human carcinogen.

4.10.2.6. Environmental issues related with plastics

Dear student, Plastics are durable and degrade very slowly; the molecular bonds that make plastic so durable make it equally resistant to natural processes of degradation. Since the 1950s,

one billion tons of plastic have been discarded and may persist for hundreds or even thousands of years. In some cases, burning plastic can release toxic fumes. Burning the plastic polyvinyl chloride (PVC) may create dioxin. Also, the manufacturing of plastics often creates large quantities of chemical pollutants.

The biggest threat to the conventional plastics industry is most likely to be environmental concerns, including the release of toxic pollutants, greenhouse gas, litter, biodegradable and non-biodegradable landfill impact as a result of the production and disposal of petroleum and petroleum-based plastics. Of particular concern has been the recent accumulation of enormous quantities of plastic trash in ocean gyres.

4.11 Natural and synthetic fibers

Dear student, in the previous content you have learnt the difference between Natural and synthetic Rubber now you learn about fibers and classes of fibers. What are fibers? Let warm up your self with the following activities.



Learning task 4.11



- a) Define fiber
- b) List the basic classes of fibers
- c) Compare and contrast natural fiber and synthetic fibers
- d) Give major uses of fibers

4.11.1 Fibers

Fiber is a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread. They are very important in the biology of both plants and animals, for holding tissues together.

Human uses for fibers are diverse. They can be spun into filaments, string or rope, used as a component of composite materials, or matted into sheets to make products such as paper or felt. Fibers are often used in the manufacture of other materials. The strongest engineering materials

are generally made as fibers, for example carbon fiber and Ultra-high-molecular-weight polyethylene.

4.11.2 Natural fibers: Natural fibers include those produced by plants, animals, and geological processes. They are biodegradable over time.

Dear student, fibers can be classified according to their origin; as fiber, Mineral, Animal and Vegetable fibers

- **Vegetable fibers** are generally based on arrangements of cellulose, often with lignin: examples include cotton, hemp, jute, flax, ramie, and sisal. Plant fibers are employed in the manufacture of paper and textile (cloth), and dietary fiber is an important component of human nutrition.
- **Wood fiber**, distinguished from vegetable fiber, is from tree sources. Forms include groundwood, thermomechanical pulp (TMP) and bleached or unbleached kraft or sulfite pulps. Kraft and sulfite, also called sulphite, refer to the type of pulping process used to remove the lignin bonding the original wood structure, thus freeing the fibers for use in paper and engineered wood products such as fiberboard.
- **Animal fibers** consist largely of particular proteins. Instances are spider silk, sinew, catgut, wool and hair such as cashmere, mohair and angora, fur such as sheepskin, rabbit, mink, fox, beaver, etc.
- **Mineral fibers** comprise asbestos. Asbestos is the only naturally occurring long mineral fiber. Short, fiber-like minerals include wollastonite, attapulgite and halloysite.

4.11.3 Synthetic or man-made fibers: generally come from synthetic materials such as petrochemicals. But some types of synthetic fibers are manufactured from natural cellulose, including rayon, modal, and the more recently developed Lyocell. Cellulose-based fibers are of two types, regenerated or pure cellulose such as from the cupro-ammonium process and modified cellulose such as the cellulose acetates. Fiber classification in reinforced plastics falls into two classes:

(i) Short fibers, also known as discontinuous fibers, with a general aspect ratio (defined as the ratio of fiber length to diameter) between 20 to 60, and

(ii) Long fibers, also known as continuous fibers, the general aspect ratio is between 200 to 500.

4.11.3.1 Polymer fibers

Polymer fibers are a subset of man-made fibers, which are based on synthetic chemicals (often from petrochemical sources) rather than arising from natural materials by a purely physical process. These fibers are made from:

- PET or PBT polyester
- Polyamide nylon
- Phenol-formaldehyde (PF)
- polyvinyl alcohol fiber (PVA) vinyon
- Polyvinyl chloride fiber (PVC) vinyon
- Polyolefins (PP and PE) olefin fiber

4.11.3.2 Microfibers

Microfibers in textiles refer to sub-denier fiber (such as polyester drawn to 0.5 dn). Microfibers in technical fibers refer to ultra fine fibers (glass or meltblown thermoplastics) often used in filtration.

Newer fiber designs include extruding fiber that splits into multiple finer fibers. Most synthetic fibers are round in cross-section, but special designs can be hollow, oval, star-shaped or trilobal. The latter design provides more optically reflective properties.

4.11.3.3 Polyamides

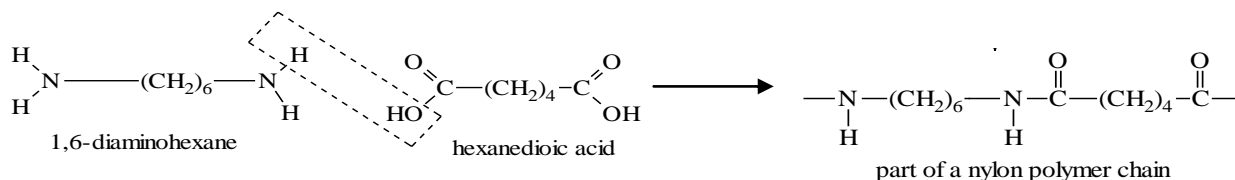
These involve the linkage of two monomers through the amide linkage as in proteins (e.g. silk). The real star of the plastics industry in the 1930s was polyamide (PA), far better known by its trade name **nylon**. Nylon was the first purely synthetic fiber, introduced by DuPont Corporation at the 1939 World's Fair in New York City. In 1927, DuPont had begun a secret development project designated Fiber66, under the direction of Harvard chemist Wallace Carothers and chemistry department director Elmer Keiser Bolton. Carothers had been hired to perform pure

research, and he worked to understand the new materials' molecular structure and physical properties. He took some of the first steps in the molecular design of the materials.

His work led to the discovery of synthetic nylon fiber, which was very strong but also very flexible. The first application was for bristles for toothbrushes. However, Du Pont's real target was silk, particularly silk stockings. Carothers and his team synthesized a number of different polyamides including polyamide 6.6 and 4.6, as well as polyesters.

Nylon 66 is a material manufactured by condensation polymerization. Nylons still remain important plastics, and not just for use in fabrics. In its bulk form it is very wear resistant, particularly if oil-impregnated, and so is used to build gears, plain bearings, and because of good heat-resistance, increasingly for under-the-hood applications in cars, and other mechanical parts

Nylon 6,6 a polyamide



4.11.3.4 Uses of polyamides

The main use of polyesters and polyamides is as fibres in clothing. Most clothing now has a degree of manufactured fibres woven into the natural material (such as cotton). This gives the material more desirable characteristics, such as stretchiness, and better washability. As it is known proteins are also polyamides, you must know how the linkage works with natural polymers such as proteins.



Chapter summary



- A **polymer** is a large molecule (macromolecule) composed of repeating structural units. These subunits are typically connected by covalent chemical bonds
- Polymers are evident all around us. Polymer characteristics depend on the type of monomer and the intermolecular bonds operating.
- Polymers can be classified into three types: Linear polymers, Branched polymers and Three-dimensional cross-linked polymers
- Classifications of polymers are based upon Polymer Structure. For example polymers can be Homochain or Hetrochain polymers.
- Homochain polymers Polymers having all carbon atoms along their backbone are important examples of homochain polymers.
- Heterochain polymers contain more than one atom type in their backbone are grouped according to the types of atoms and chemical groups
- Addition polymerization is a polymerization process that is produced by successive addition reactions. A carbon – carbon double bond is needed in the monomer.
- In condensation polymers , the molecular formula of the structural unit (or units) lacks certain atoms present in the monomer from which it is formed, or to which it may be degraded by chemical means. It involves 2 monomers that have different functional groups. They also involve the ***elimination of water or another small molecule***.
- Based on polymer structure, the properties of a given polymer can be varying. For example, Synthetic polymers may consist of both ***crystalline and amorphous regions***.
- A plastic is a material that contains as an essential ingredient, an organic substance of a large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow.
- A thermoplastic material is one which can be softened and molded on heating. They are elastic and flexible above a certain glass transition temperature.
- Thermosetting plastics (thermosets) are polymer materials that cure or are made strong by addition of elements (e.g. sulphur) or addition of energy in form of heat (normally above 200°C) through some chemical reaction.
- Molding of a plastic is a process of making a hollow form or matrix into which a plastic material is placed and which imparts to the material its final shape as a finished article. The common molding of plastics into articles is ***Blow molding***.

- Polystyrene is a rigid, brittle, inexpensive plastic that has been used to make plastic model kits and similar knick-knacks.
- Polyvinyl Chloride (PVC), has side chains incorporating chlorine atoms, which form strong bonds. PVC in its normal form is stiff, strong, heat and weather resistant, and is now used for making plumbing, gutters, house siding, enclosures for computers and other electronics gear.
- Bakelite is a thermosetting phenol formaldehyde resin, formed from an elimination reaction of phenol with formaldehyde, usually with wood flour filler.
- All rubberlike materials are polymers, which are high molecular weight compounds consisting of long chains of one or more types of molecules, such as monomers.
- Vulcanization (or curing) produces chemical links between the loosely coiled polymeric chains; elasticity occurs because the chains can be stretched and the crosslinks cause them to spring back when the stress is released.
- Natural rubber is an elastomer (an elastic hydrocarbon polymer) that was originally derived from *latex*, a milky colloidal suspension found in the sap of some plants.
- **Synthetic rubber** is any type of artificially made polymer material, which acts as an elastomer.
- An elastomer is a material with the mechanical (or material) property that it can undergo much more elastic deformation under stress, than most materials and still return to its previous size without permanent deformation.
- **Fiber** is a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread. They are very important in the biology of both plants and animals, for holding tissues together.
- Natural fibers: Natural fibers include those produced by plants, animals, and geological processes.
- **Synthetic or man-made fibers** generally come from synthetic materials such as petrochemicals.



Self test exercises



1. Polymers are evident all around us; explain the difference between natural polymer and synthetic polymer
2. Compare and contrast natural polymers, biopolymers and synthetic polymers
3. Discuss how classification of polymers is based on Nomenclature of polymers
4. The common methods of polymerization are addition polymerization and condensation polymerization
 - a) Explain the difference between Addition and condensation polymerization
 - b) Give examples of polymers that are formed by Addition and condensation polymerization
5. Explain how polymer structure can affect the properties of a polymer
6. a) Explain the basic classification of plastics
 - b) Compare and contrast thermoplastics and thermosetting
7. PE, PVC and Bakelite are the common plastic material that are used for different activities
 - a) Explain how PE, PVC and Bakelite are prepared?
 - b) Mention the major properties of PE, PVC and Bakelite
8. Explain the Chemistry and Properties of rubber
9. Write all the equations using the structural formula of the main raw materials and products for the main reactions that take place during the manufacture of phthalic anhydride and adipic acid.
10. Name 10 materials that you use daily which are made of synthetic organic polymers
11. Vinyl chloride undergoes copolymerization with 1,1-dichloroethylene to form a polymer, commercially known as Saran. Write equations for this polymerisation.
12. Fiber is a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread.
 - a) List the basic classes of fibers
 - b) Compare and contrast natural fiber and synthetic fibers
 - c) Give major uses of fibers



Unit Introduction

Dear student, this chapter deals with Sucrose Industry. We will also discuss further about Manufacture of cane sugar, Manufacture of sucrose from Beet Root, Quality control in sugar industry and Testing of sugar



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define cane sugar
- Explain how sucrose is manufactured from Beet root
- Discuss how the quality of sugar is controlled
- Mention common Methods that are used for testing sugar

5.1 Introduction

Dear student, you are familiar with sugar, what are the main raw materials for the manufacturing process of sugar? How the quality of sugar can checked? How a given sample is tested to check its sugar content? Such type of common questions can be raised.

5.1.1 Raw Materials for sugar industry

Sugar is a broad term applied to a large number of carbohydrates present in many plants and characterized by a more or less sweet taste. The primary sugar, glucose, is a product of photosynthesis and occurs in all green plants. In most plants, the sugars occur as a mixture that cannot readily be separated into the components. In the sap of some plants, the sugar mixtures are condensed into syrup. Juices of **sugarcane** (*Saccharum officinarum*) and **sugar beet** (*Beta vulgaris*) are rich in pure sucrose, although beet sugar is generally much less sweet than cane sugar. These two sugar crops are the main sources of commercial sucrose.

5.2. Manufacture of Cane sugar

Dear student, in the introduction part of this chapter, you have introduced that the main sources of commercial sucrose are sugarcane and sugar beet. Now under this main content you learn the manufacturing process of cane sugar. Can you mention the manufacturing process of cane sugar?

Let warm up your self with the following activities.



Learning task 5.2



- a) List the main manufacturing process of Cane sugar
- b) Discuss how planting and harvesting of sugar cane is processed
- c) Explain how juice of a sugar cane is purified

The sugarcane is a thick, tall, perennial grass that flourishes in tropical or subtropical regions. Sugar synthesized in the leaves is used as a source of energy for growth or is sent to the stalks for storage. It is the sweet sap in the stalks that is the source of sugar as we know it. The reed accumulates sugar to about 15 percent of its weight. Other sugar crops include sweet sorghum, sugar maple, honey, and corn sugar. The types of sugar used today are white sugar (fully refined sugar), composed of clear, colorless or crystal fragments; or brown sugar, which is less fully refined and contains a greater amount of treacle residue, from which it obtains its color.

5.2.1 The Manufacturing process of Cane sugar

5.2.1.1 Planting and harvesting

Sugarcane takes about seven months to mature in a tropical area and about 12-22 months in a subtropical area. At this time, fields of sugarcane are tested for sucrose, and the most mature fields are harvested first. The harvested cane stalks are loaded mechanically into trucks or railroad cars and taken to mills for processing into raw sugar. For example, in the United States, harvesting of both cane and sugar beet is done primarily by machine, although in some states it is also done by hand. The harvested cane stalks and beets are loaded mechanically into trucks or railroad cars and taken to mills for processing into raw sugar. Once there, they are cleaned, washed, milled to extract juice, filtered, and purified. The result is a clear, sugar-filled juice. **Therefore, it is grown in tropical or subtropical areas.**

5.2.1.2 Preparation and processing

After the cane arrives at the mill yards, it is mechanically unloaded and excessive soil and rocks are removed. The cane is cleaned by flooding the carrier with warm water or by spreading the cane on agitating conveyors that pass through strong jets of water and combing drums (to remove larger amounts of rocks, trash, and leaves, etc.). At this point, the cane is clean and ready to be milled. When the beets are delivered at the refinery, they are first washed and then cut into strips.

After being purified, the clear juice undergoes vacuum evaporation to remove most of the water. In this process, four vacuum-boiling cells are arranged in series so that each succeeding cell has a higher vacuum. The vapors from one body can thus boil the juice in the next one, a method called *multiple-effect evaporation*. Next, the syrupy solution is vacuum-crystallized to form sugar crystals. The remaining liquid is removed using centrifuging and drying, and the sugar is packaged. Water at about 175 degrees Fahrenheit (79.4 degrees Celsius) and sprayed with hot water countercurrently to remove the sucrose.

5.2.1.3 Juice extraction pressing

Two or three heavily grooved crusher rollers break the cane and extract a large part of the juice, or swing-hammer type shredders (1,200 RPM) shred the cane without extracting the juice. Revolving knives cutting the stalks into chips are supplementary to the crushers. (In most countries, the shredder precedes the crusher.) A combination of two, or even all three, methods may be used. The pressing process involves crushing the stalks between the heavy and grooved metal rollers to separate the fiber (*bagasse*) from the juice that contains the sugar.

As the cane is crushed, hot water (or a combination of hot water and recovered impure juice) is sprayed onto the crushed cane countercurrently as it leaves each mill for diluting. The extracted juice, called *vesou*, contains 95 percent or more of the sucrose present. The mass is then diffused, a process that involves finely cutting or shredding the stalks. Next, the sugar is separated from the cut stalks by dissolving it in hot water or hot juice.

5.2.1.4 Purification of juice-Clarification and evaporation

Clarification (or defecation) process is designed to remove both soluble and insoluble impurities (such as sand, soil, and ground rock) that have not been removed by preliminary screening. The process employs lime and heat as the clarifying agents. Milk of lime (about one pound per ton of cane) neutralizes the natural acidity of the juice, forming insoluble lime salts. Heating the lime juice to boiling coagulates the albumin and some of the fats, waxes, and gums, and the precipitate formed entraps suspended solids as well as the minute particles.

To concentrate this clarified juice, about two-thirds of the water is removed through vacuum evaporation. Generally, four vacuum-boiling cells or bodies are arranged in series so that each succeeding body has a higher vacuum (and therefore boils at a lower temperature). The vapors from one body can thus boil the juice in the next one—the steam introduced into the first cell does what is called *multiple-effect evaporation*. The vapor from the last cell goes to a condenser. The syrup leaves the last body continuously with about 65 percent solids and 35 percent water.

5.2.1.5 Crystallization

Crystallization is the next step in the manufacture of sugar. Crystallization takes place in a single-stage vacuum pan. The syrup is evaporated until saturated with sugar. As soon as the saturation point has been exceeded, small grains of sugar are added to the pan, or "strike." These small grains, called *seed*, serve as nuclei for the formation of sugar crystals. Additional syrup is added to the strike and evaporated so that the original crystals that were formed are allowed to grow in size.

The growth of the crystals continues until the pan is full. When sucrose concentration reaches the desired level, the dense mixture of syrup and sugar crystals, called *massecuite*, is discharged into large containers known as crystallizers. Crystallization continues in the crystallizers as the massecuite is slowly stirred and cooled. Massecuite from the mixers is allowed to flow into centrifugals, where the thick syrup, or molasses, is separated from the raw sugar by centrifugal force.

5.2.1.6 Centrifugation

The high-speed centrifugal action used to separate the massecuite into raw sugar crystals and molasses is done in revolving machines called centrifugals.

A centrifugal machine has a cylindrical basket suspended on a spindle, with perforated sides lined with wire cloth, inside which are metal sheets containing 400 to 600 perforations per square inch. The basket revolves at speeds from 1,000 to 1,800 RPM. The raw sugar is retained in the centrifuge basket because the perforated lining retains the sugar crystals. The mother liquor, or molasses, passes through the lining (due to the centrifugal force exerted). The final molasses (*blackstrap molasses*) containing sucrose, reducing sugars, organic nonsugars, ash, and water, is sent to large storage tanks.

Once the sugar is centrifuged, it is "cut down" and sent to a granulator for drying. In some countries, sugarcane is processed in small factories without the use of centrifuges, and a dark-brown product (noncentrifugal sugar) is produced. Now days, Centrifugal sugar is produced in many countries while noncentrifugal sugar is in few countries.

5.2.1.7 Drying and packaging

Damp sugar crystals are dried by being tumbled through heated air in a granulator. The dry sugar crystals are then sorted by size through vibrating screens and placed into storage bins. Sugar is then sent to be packed in the familiar packaging we see in grocery stores, in bulk packaging, or in liquid form for industrial use.

5.2.1.8 Byproducts

The **bagasse** produced after extracting the juice from sugar cane is used as fuel to generate steam in factories. Increasingly large amounts of bagasse are being made into paper, insulating board, and hardboard, as well as furfural, a chemical intermediate for the synthesis of furan and tetrahydrofuran. The beet tops and extracted slices as well the **molasses** are used as feed for cattle and for the manufacturing of ethanol.

5.3 Manufacture of sucrose from Beet root

Dear student, you have introduced the main manufacturing of cane sugar. Now under this main content you learn the manufacturing of sucrose from Beet root. Do you know sugar beet? Its uses? Let warm up your self with the following activities.



Learning task 5.3



- a) List the main Manufacturing process of sucrose from Beet root
- b) Discuss how Planting and harvesting of Beet root is processed
- c) Explain how juice of a Beet root is purified

5.3.1 Introduction

Sugar beet, a cultivated plant of *Beta vulgaris*, is a plant whose tuber contains a high concentration of sucrose. It is grown commercially for sugar production. Sugar beets and other *B. vulgaris* cultivars such as beetroot and chard share a common wild ancestor, the sea beet (*Beta vulgaris maritima*.) The European Union, the United States, and Russia are the world's three largest sugar beet producers, although only the European Union and Ukraine are significant exporters of sugar from beets.

Until the latter half of the 20th century, sugar beet production was highly labor-intensive, as weed control was managed by densely planting the crop, which then had to be manually thinned with a hoe two or even three times during the growing season. Harvesting also required many workers. Although the roots could be lifted by a plough-like device which could be pulled by a horse team, the rest of the preparation was by hand. Today, mechanical sowing, herbicide applications for weed control and mechanical harvesting has removed this reliance on numerous workers. Harvesting is now entirely mechanical. Depending on the local climate, it may be carried out over the course of a few weeks or be prolonged throughout the winter months.

5.3.2 Processing of Sugar beet

5.3.2.1 Reception

After they are harvested, beets are hauled to a factory. For example, in the U.K., beets are transported by a hauler, or by a tractor and a trailer by local farmers. Now days, Railways and boats are no longer used except in few countries.

5.3.2.2 Diffusion

After reception at the processing plant, the beet roots are washed, mechanically sliced into thin strips called *cossettes*, and passed to a machine called a diffuser to extract the sugar content into a water solution. Diffusers are long vessels of many metres in which the beet slices go in one direction while hot water goes in the opposite direction. The movement may either be by a rotating screw or the whole unit rotates, and the water and cossettes move through internal chambers.

5.3.2.3 Carbonatation

Carbonatation is a procedure which removes impurities from raw juice before it undergoes crystallization. First, the juice is mixed with hot milk of lime (a suspension of calcium hydroxide in water). This treatment precipitates a number of impurities, including multivalent anions such as sulfate, phosphate, citrate and oxalate, which precipitate as their calcium salts and large organic molecules such as proteins, saponins and pectins, which aggregate in the presence of multivalent cations. In addition, the alkaline conditions convert the simple sugars, glucose and fructose, along with the amino acid glutamine, to chemically stable carboxylic acids. Left untreated, these sugars and amines would eventually frustrate crystallization of the sucrose.

Next, carbon dioxide is bubbled through the alkaline sugar solution, precipitating the lime as calcium carbonate (chalk). The chalk particles entrap some impurities and absorb others. A recycling process builds up the size of chalk particles and a natural flocculation occurs where the heavy particles settle out in tanks (clarifiers). A final addition of more carbon dioxide precipitates more calcium from solution; this is filtered off, leaving a cleaner, golden light-brown sugar solution called *thin juice*.

Before entering the next stage, the thin juice may receive soda ash to modify the pH and sulphitation with a sulfur-based compound to reduce color formation due to decomposition of monosaccharides under heat.

5.3.2.4 Evaporation

The thin juice is concentrated via multiple-effect evaporation to make a *thick juice*, roughly 60% sucrose by weight and similar in appearance to pancake syrup. Thick juice can be stored in tanks for later processing, reducing load on the crystallization plant.

5.3.2.5 Crystallization

Thick juice is fed to the crystallizers. Recycled sugar is dissolved into it, and the resulting syrup is called mother liquor. The liquor is concentrated further by boiling under vacuum in large vessels (the so-called vacuum pans), seeded with fine sugar crystals. These crystals grow, as sugar from the mother liquor forms around them. The resulting sugar crystal and syrup mix is called a *massecuite*, from "cooked mass" in French. The massecuite is passed to a centrifuge where the liquid is removed from the sugar crystals. Remaining syrup is rinsed off with water and the crystals dried in a granulator using warm air.

The remaining syrup is fed to another crystallizer from which a second batch of sugar is produced. This sugar ("raw") is of lower quality with a lot of color and impurities and is the main source of the sugar that is dissolved again into the mother liquor. The syrup from the raw is also sent to a crystallizer. From this a very low-quality sugar crystal is produced that is also redissolved. The syrup separated is molasses, which still contains sugar but contains too much impurity to undergo further processing economically. Actual procedure may vary from the above description, with different recycling and crystallization processes.

5.3.2.6 Other uses

Besides, production of sucrose, beet root can also be used for in different industries. Such as in Beverages, Sugar beet syrup, Alternative fuel and etc.

5.4 Quality Control of Sugars

Dear student, you have introduced how sucrose is manufactured from sugar cane and sugar beet. Therefore, in order to have a standard sucrose or sugar there is a need of quality control. Can you explain the advantage of quality control in sugar industry? Let warm up your self with the following activities.



Learning task 5.4



- a) Define quality control
- b) Discuss how we can control the quality of sugar in sugar industry
- c) Mention of major techniques that can help to keep the quality a given product in an industry

Dear student, Mill sanitation is an important factor in quality control measures. Bacteriologists have shown that a small amount of sour bagasse can infect the whole stream of warm juice flowing over it. Modern mills have self-cleaning troughs with a slope designed in such a way that bagasse does not hold up but flows out with the juice stream. Therefore, strict measures have to be taken for insect and pest controls.

Because cane spoils relatively quickly, great steps have been taken to automate the methods of transportation and get the cane to the mills as quickly as possible. Maintaining the high quality of the end-product means storing brown and yellow refined sugars (which contain two percent to five percent moisture) in a cool and relatively moist atmosphere, so that they continue to retain their moisture and do not become hard.

5.5 Testing of Sugar

Dear student, you have introduced how sucrose can be manufactured from sugar cane and sugar beet. Besides you have learnt how quality control can be applied in sugar industry. Now under this main content you learn how sugar can be tested. Can you mention some techniques that can be used to test sugar? , let warm up your self with the following activities.



Learning task 5.5



- a) Mention some methods that can be used to test sugar
- b) What type of methods are common to test sugar
- c) Explain the advantages of food chemistry testing and testing sugar

5.5.1 Food Chemistry Testing

Studies to learn those chemical processes taking place inside food tell us what is safe to eat, make sure the quality is consistent and even appetizing - studies that do flavor and texture analyses, aroma, temperature effects and calorie analysis.

5.5.2 Testing for Sugar

Carbohydrates make up a group of organic compounds which supply the body with energy and include **sugars** and **starches**. Some starches provide your body with the roughage or fiber to aid digestion. There are various methods for testing of sugar. The main ones include *Chemical methods and enzymatic methods*. Some of the chemical methods and enzymatic methods are discussed below.

5.5.2.1 Benedict's reagent

Benedict's reagent is used as a test for the presence of reducing sugars. This includes all monosaccharides and the disaccharides, lactose and maltose. Even more generally, Benedict's test will detect the presence of aldehydes (except aromatic ones), and alpha-hydroxy-ketones, including those that occur in certain ketoses. Thus, although the ketose fructose is not strictly a reducing sugar, it is an alpha-hydroxy-ketone, and gives a positive test because it is converted to the aldoses glucose and mannose by the base in the reagent.

One litre of Benedict's reagent can be prepared from 100 g of anhydrous sodium carbonate, 173 g of sodium citrate and 17.3 g of copper(II) sulfate pentahydrate. It is often used in place of Fehling's solution. Benedict's reagent contains blue copper(II) ions (Cu^{2+}) which are reduced to copper(I) ions (Cu^+). These are precipitated as red copper(I) oxide which is insoluble in water.

To test for the presence of monosaccharides and reducing disaccharide sugars in food, the food sample is dissolved in water, and a small amount of Benedict's reagent is added. During a water bath, which is usually 4–10 minutes, the solution should progress in the colors of blue (with no glucose present), green, yellow, orange, red, and then brick red or brown (with high glucose present). A colour change would signify the presence of glucose. The common disaccharides

lactose and maltose are directly detected by Benedict's reagent, because each contains a glucose with a free reducing aldehyde moiety, after isomerization.

Sucrose (table sugar) contains two sugars (fructose and glucose) joined by their glycosidic bond in such a way as to prevent the glucose isomerizing to aldehyde, or the fructose to alpha-hydroxy-ketone form. Sucrose is thus a non-reducing sugar which does not react with Benedict's reagent. Sucrose indirectly produces a positive result with Benedict's reagent if heated with dilute hydrochloric acid prior to the test, although after this treatment it is no longer sucrose. The acidic conditions and heat break the glycosidic bond in sucrose through hydrolysis. The products of sucrose decomposition are glucose and fructose, both of which can be detected by Benedict's reagent, as described above.

Starches do not react or react very poorly with Benedict's reagent, due to the relatively small number of reducing sugar moieties, which occur only at the ends of carbohydrate chains. Inositol (myo-inositol) is another carbohydrate which produces a negative test.

Benedict's reagent can be used to test for the presence of glucose in urine. Glucose found to be present in urine is an indication of diabetes mellitus. Once a reducing sugar is detected in urine, further tests have to be undergone in order to ascertain which sugar is present. Only glucose is indicative of diabetes.

5.5.2.2 Fehling's solution

Fehling's solution is a chemical test used to differentiate between water-soluble aldehyde and ketone functional groups, and as a test for monosaccharides. The test was developed by German chemist Hermann von Fehling in 1849.

Fehling's can be used to determine whether a carbonyl-containing compound is an aldehyde or a ketone. The bistartratocuprate(II) complex in Fehling's solution is an oxidizing agent and the active reagent in the test. The compound to be tested is added to the Fehling's solution and the mixture is heated. Aldehydes are oxidized, giving a positive result, but ketones do not react, unless they are alpha-hydroxy-ketones. The bistartratocuprate(II) complex oxidizes the aldehyde to a carboxylate anion, and in the process the copper(II) ions of the complex are reduced to

copper(I) ions. Red copper(I) oxide then precipitates out of the reaction mixture, which indicates a positive result i.e. that redox has taken place (this is the same positive result as with Benedict's solution. A negative result is the absence of the red precipitate; it is important to note that Fehling's will not work with aromatic aldehydes; in this case Tollens' reagent should be used.

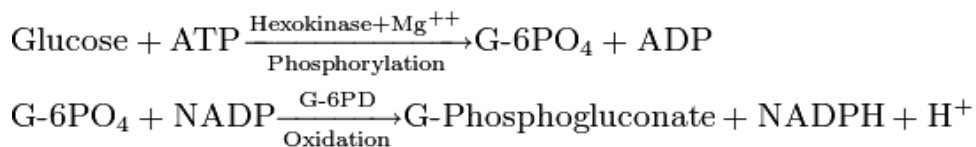
Fehling's test can be used as a generic test for monosaccharides. It will give a positive result for aldose monosaccharides (due to the oxidisable aldehyde group) but also for ketose monosaccharides, as they are converted to aldoses by the base in the reagent, and then give a positive result. For this reason, Fehling's reagent is sometimes referred to as a general test for monosaccharides.

5.5.2.3 Enzymatic methods

a) Glucometer

Home monitoring blood glucose assay method uses a strip impregnated with a glucose oxidase reagent

b. Hexokinase



NADP as cofactor; NADPH (reduced product) is measured in 340 nm

This method is more specific than glucose oxidase method due to G-6 PO₄, which inhibits interfere product

5.5.3 Product

The final sugar is white and ready for use, whether in the kitchen or by an industrial user such as a soft drink manufacturer. As for raw sugar production, because one cannot get all the sugar out of the juice, there is a sweet by-product made: beet molasses. This is usually turned into a cattle food or is sent to a fermentation plant such as a distillery where alcohol is made. It does not have the same quality smell and taste as cane molasses so cannot be used for rum production.

5.5.4 Effluent treatment

The Effluent (waste water) from sugar factory contains organic materials, which will have to be contained and treated prior to disposal to the environment. The objective of treatment of such effluent is to reduce the biological and chemical oxygen demands to allowable levels. This can be achieved by carrying out primary clarification, aeration, fuel clarification and sludge drying. The sludge so obtained can be used as organic fertilizer.



Chapter summary



- Sugar is a broad term applied to a large number of carbohydrates present in many plants and characterized by a more or less sweet taste.
- Juices of sugarcane (*Saccharum officinarum*) and sugar beet (*Beta vulgaris*) are rich in pure sucrose, although beet sugar is generally much less sweet than cane sugar. These two sugar crops are the main sources of commercial sucrose.
- The Manufacturing process of Cane sugar involves:
 - ✓ Planting and harvesting
 - ✓ Preparation and processing
 - ✓ Juice extraction and pressing
 - ✓ Purification of juice
 - ✓ Crystallization
 - ✓ Centrifuging
 - ✓ Drying and packaging
 - ✓ Byproducts
- Sugar beet, a cultivated plant of *Beta vulgaris*, is a plant whose tuber contains a high concentration of sucrose. It is grown commercially for sugar production.
- Processing of Sugar beet involves: Reception, Diffusion, Carbonatation, Evaporation, and Crystallization
- Testing the Quality of sugar in industry is important parameter for sustainable sugar production and sustainable market.



Self test exercises



1. Explain the manufacturing process of cane sugar and beet sugar
2. Compare and contrast the manufacturing process of cane sugar and beet sugar
3. Discuss how the quality of sugar is controlled
4. In sugar industry different chemicals are added for different activities. Mention some common chemicals that are used for juice extraction and purification
5. If somebody becomes a manager of sugar Factory; what will be his responsibility in terms of:
 - a) To have good quality of sugar
 - b) To be environmentally friendly
 - c) To get sustainable profit



Unit Introduction

Dear student, this chapter deals with Oils, Fats and Detergents. We will also discuss further about Introduction to oils and fats, Properties of oils and fats, Classification of oils, Manufacture of vegetable oils, Animal fats and oils, Analysis of oils and fats, Hydrogenation of oils, Manufacture of soap and Introduction to detergents



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define Oils, Fats and Detergents
- Mention Properties of oils and fats
- List the major classification of oils
- Discuss how vegetable oils are manufactured
- Mention properties of Animal fats and oils
- Explain how fats and oils are analyzed
- Discuss why oils are hydrogenated
- List the manufacturing process of soap
- Compare and contrast soap and detergents

6.1 Introduction to oils and fats

Dear student, oils and fats are some of important substances to human being. Therefore, it is necessary to study their source, properties, manufacturing process and specific uses. Now under this main content you learn their distribution and their uses. What do you know about oils and fats? Let warm up your self with the following activities.



Learning task 6.1



- a) Define oils and fats
- b) Mention the major source of oils and fats
- c) List the major uses of oils and fats

Dear student, Fats and oils are found widely distributed in nature, in both the plant and the animal kingdoms. Fats and oils are mixtures of the glycerides of various fatty acids. The animal fats were first consumed as food, but it was not long before the burning of the oils for light and heat was learned. Obtaining oils from vegetable sources is of ancient origin, for the natives in the tropical regions of the globe have long been removing these oils from various nuts after drying them in the sun. The first chemical reaction applied to fats and oils (excluding oxidation in burning) were that of saponification, to give soap.

The fats and oils have always had an essential role as food for mankind. In addition, however, our modern industrial world has found many important applications for them. There are broad classification for the fats and oils: edible and inedible. The various edible oils, cottonseed, olive, soybean, corn, etc., are employed for salad dressings, other table uses, and for cooking purposes.

6.2. Properties of oils and fats

Dear student, you have learnt that oils and fats are some of important substances to human being. Therefore, it is necessary to study their properties. Now under this main content you learn Properties of oils and fats. Can you mention some of the properties of oils and fats? Let warm up your self with the following activities.



Learning task 6.2



- a) Mention the major properties of fats and oils
- b) Compare and contrast Chemical and Physical Characteristics of fats and oils

6.2.1 Physical properties of oils and fats

The common physical properties of oils and fats are that they float on water but are not soluble in it; they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue, i.e., ash. No other class of substances has the chemical properties of the fats and oils; but many possess similar physical ones, e.g., mineral oils, earth-wax (ozocerite), paraffin, animal waxes like spermaceti or beeswax, vegetable waxes like carnauba or candelilla wax, volatile or essential vegetable oils like the oils of thyme, of cloves, of cedar, and attar of roses. None of these substances furnishes both glycerin and fatty acids; none of them has nutritive value; none of them will be considered further in this treatise.

6.2.2 Chemical properties of oils and fats

The common chemical characteristic of oils and fats are capable of serving as foodstuffs may be decomposed into glycerin and one or more acids of the class known to chemists as fatty acids. Chemists designate as acids a class of substances which have an acid or sour taste; contain the element hydrogen; and act upon metals, hydrogen being evolved and its place being taken by the metal. Fats and oils are substances which consist always of chemical combinations of glycerin with certain fatty acids, and which may serve as foods.

The distinction between a fat and oil is purely an accidental one depending upon the environment in which the substance happens to be placed. If the substance is solid at ordinary temperatures, it

is termed a fat; if fluid, an oil. This is merely a distinction of convenience, since all oils are solidified at lower temperatures and all fats melted at higher temperatures. Obviously, the dividing line that holds for a cool climate would not hold for a hot one. In each climate, however, the distinction is of importance in industrial and in culinary uses; it has also some importance in nutrition, since fats are somewhat less digestible than oils.

6.3. Classification of oils

Dear student, you have learnt that the common physical and chemical properties of oils and fats. Now under this main content you learn Classification of oils. Can you explain how oils are classified? Let warm up your self with the following activities.



Learning task 6.3



- a) List the three major classifications of oils
- b) Compare and contrast vegetable oils, animals' oils and fats, and waxes

For purposes of discussion of the various technical aspects, the three classical divisions of the general subject of oils, fats, and waxes will be retained. There are three major classifications of oils. These are: *vegetable oils, animals' oils and fats, and waxes*. Under each of these headings the general methods of manufacture will be discussed for the most important of the illustrative individual members. The two general methods employed in obtaining vegetable fats and oils are expression and solvent extraction or a combination of the two. However, solvent extraction is increasing in use.

6.4 Animal and Vegetable Sources

Dear student, you have learnt the three major classifications of oils are: vegetable oils, animals' oils and fats, and waxes. Now under this main content you learn Animal and Vegetable Sources for oils and fats. Therefore, let warm up your self with the following activities.



Learning task 6.4



- a) Give example of oils and fats which are animal source
- b) Give example of oils and fat which are vegetable source
- c) Compare and contrast animal source and vegetable source oils and fats

Dear student, Animal fats and oils are derived both from terrestrial and marine animals. Marine fats include liver oils, blubber oils, and fish oils. The different types of marine fats, which in practice are often mixed, have been of great importance in the past and still possess considerable significance. Some of these serve special purposes, such as codliver oil; others are used to some extent as foodstuffs; but for the most part they serve industrial uses.

With two important exceptions animal fats are obtained from carcasses. These two exceptions are butter and the fat of the yolks of eggs. The fats from the different parts and organs of a given animal differ somewhat in their properties. As a rule, the fat from the interior of the animal is somewhat firmer than the fat from near the body surface, i.e., it melts at a somewhat higher temperature. Furthermore, under certain conditions the feed of the animal affects the physical properties of the carcass fat more or less. Animals fattened upon a diet containing much oil -- for example, peanuts -- tend to produce softer carcass fats than animals of the same species fattened upon a diet containing relatively little oil -- for example, corn (maize).

Vegetable fats and oils are found in greatest abundance in fruits and seeds. While fats and oils do occur in the roots, stalks, branches, and leaves of plants, they are rarely present in these organs in quantities large enough for commercial purposes. In some seeds and fruits, however, the fat content is great -- in several cases as high as 35 per cent; in dried coconuts 65 per cent -- and these are the commercial sources of vegetable fats. In some seeds the fat is practically confined to the germ or embryo; this is the fact in most of the cereals. It is usually only a small part of the

seed. The remainder of the seed consists mainly of reserve food material with the help of which the embryo grows into the plantlet which, as it develops roots, is enabled to draw its nourishment from the soil. For example, the olive contains a large amount of fat in the pulp surrounding the kernel and only a smaller amount in the kernel itself, while in the oil palm both the pulp and the kernel contain large amounts.

6.5. Manufacture of vegetable oils

Dear student, you have learnt the main source of oils and fats can be either Animal or Vegetable. Now under this main content you learn Manufacture of vegetable oils. From your experience can you mention how vegetable oils are manufactured? , Let warm up your self with the following activities.



Learning task 6.5



- a) Explain how vegetable oils are manufactured industrially
- b) Compare and contrast manufacturing cotton seed oil and manufacturing Soybean oil

6.5.1 Industry Description and Practices

The vegetable oil processing industry involves the extraction and processing of oils and fats from vegetable sources. Vegetable oils and fats are principally used for human consumption but are also used in animal feed, for medicinal purposes, and for certain technical applications. The oils and fats are extracted from a variety of fruits, seeds, and nuts. The preparation of raw materials includes husking, cleaning, crushing, and conditioning.

The extraction processes are generally mechanical (boiling for fruits, pressing for seeds and nuts) or involve the use of solvent such as hexane. After boiling, the liquid oil is skimmed; after pressing, the oil is filtered; and after solvent extraction, the crude oil is separated and the solvent is evaporated and recovered. Residues are conditioned (for example, dried) and are reprocessed to yield by-products such as animal feed. Crude oil refining includes degumming, neutralization, bleaching, deodorization, and further refining.

6.5.2 Manufacturing cotton seed oil by expression and solvent extraction

Solvent extraction is assuming importance in virtually all vegetable-oil recovery plants, alone or in combination with a prepressing. High -oil- content seeds, such as cotton-seed and safflower seed, usually utilize both expression and extraction in their recovery systems for higher yields. Obtaining crude vegetable and animal oils involves almost altogether only the physical changes or unit operations, but the chemical conversions are concerned in the refining and the further processing of such oils. Solvent extraction recovers up to 98% of cottonseed oil compared with 90 to 93% from screw-press expression alone.

6.5.3 Manufacturing Soybean oil by solvent extraction

The soybean preparation-seed differs slightly from cottonseed preparation. The weighed and cleaned seed are first cracked between corrugated rolls and then conditioned without significant change in moisture in a stacked cooker or a rotary steam-tube conditioner, and finally rolled to a thin flake(about 0.010in.thick). Solvent extraction can recover up to 98% of oil compared with about 80 to 90% from hydraulic or screw expression. The soybean, whose physical structure is particularly suited to solvent extraction, has been responsible for this development.

Solvent extraction is carried out in a continuous countercurrent manner through a series of extraction stages. The rate of diffusion is directly proportional to the surface area of the seed particle and in an (inverse) power function of thickness with free circulation of the solvent. After extraction, the meal is steamed to remove all solvent.

The overall processing of crude vegetable oils usually involves alkali refining, water washing and drying, bleaching, hydrogenation, and deodorizing. In the alkali method the free fatty acids are neutralized with caustic soda or soda ash, forming soaps, commonly called foots, which are removed by centrifuges, the fatty acids being recovered. The oils are bleached with adsorbent clay either batch wise or in a continuous process.

Dear student, there are various types' plant oils. Some of them are:

- **Corn oil:** - the production of corn oil differs from some of the others in certain respects. After cleaning, the corn is placed in large tanks and steeped with warm water containing SO₂, thus loosening the hull from the kernel.
- **Palm oil** is prepared from the fruit of the palm tree, which has been cultivated on plantations in Indonesia, the Malay Peninsula, and elsewhere. The palms grow naturally on the west coast of Africa.
- **Castor oil** this well-known oil is obtained from the seeds, or beans, of the castor plant found in most tropical regions. The beans contain 35 to 55 % oil, and are expressed or solvent-extracted. The finest grade of oil is reserved for medicinal purposes. The lower grades are used in the manufacture of transparent soaps, flypaper, type paper inks, and as a motor lubricant.

6.6. Animal fats and oils

Dear student, you have learnt how vegetable oils are Manufactured. Now under this main content you learn Animal fats and oils. **Can you mention, the difference between vegetable oils and animal fats and oils?**, Let warm up your self with the following activities.



Learning task 6.6



- Explain the properties of Animal fats and oils
- Discuss the physical and chemical processing of Animal fats and oils
- Compare and contrast Animal fats and oils and vegetable oils

6.6.1 Introduction

Dear student, much chemical processing, started early by hydrogenation, and now intensified by interesterification and isomerization, has improved the quality of animal fats and oils. Chemical engineering has reduced the cost of processing, particularly by changing from batch to continuous processing. Such treatment has also been applied to vegetable oils. There are various types of animal fats and oils; some of them are the following.

i) **Neat's-foot oil:** - the skin, bones, and feet of cattle (exclusive of the hoofs) are cooked or rendered in water for 10 hr to separate the fat. This is skimmed off the top of the water and, after filtering through cloth, heated in a kettle to 25⁰F for several hours. The kettle is cooled, the contents are settled, and the oil is drawn off, filtered through flannel bags, and sent to the refinery. Here the oil is grained. This requires about 2 weeks at 34⁰F. The product is pressed once, yielding pure neat's foot oil. The stearin from the first pressing is re-pressed to yield a second grade of oil. The pure variety is used for oiling watches and other fine machinery, the latter in the textile and leather industries. The stearin from the second pressing is consumed in soap.

ii) **Whale oil:**-This oil is now obtained from modern floating factory ships which catch, butcher, and process the mammals at the scene of the catch. To prepare the oil, the blubber stripped from the flesh and boiled in open digesters. The finest grade of oil separates first. It is practically odorless, very pale in color, and contains very little free fatty acids. Upon continued boiling, a second grade is obtained, and if the residue from this operation is cooked under pressure, a third grade is made available. All grades are centrifuged to clarify and dry them further before placing them in storage. The oils obtained are used in the manufacture of lard substitutes and in soap making. Both fish and whale oils contain unsaturated fatty acids of 14 to 22 carbon atoms, and as many as 6 double bonds.

iii) **Fish oils:** - Fresh menhaden sardine and salmon are cooked whole by steam for a short period and pressed. The oil is settled (or centrifuged) and winterized. The remainder of the fish is dried, pulverized, and sold as meal for feed. Each fish contains, on the average, 20% oil by weight. The oils are consumed in paints, as lubricants, and in leather and soft-soap manufacture and when sulfonated yield a variety of Turkey-red oil.

6.6.2 Processing of animal fats and oils

There is no particular method common to the processing of all animals oils and fats, though continuous (processing) is fundamentally the most important procedure from both the economical and the chemical engineering viewpoints, with these new processes applying the results of recent chemical conversions such as interesterfication and isomerization, as well as the

older hydrogenation. For both animal and vegetable oils contain processing steps in common, e.g., refining, bleaching, hydrogenating, and deodorizing. Finally, both vegetable and animal oils are raw materials for further chemical conversions to produce soaps and detergents, as well as improved lard and other fats and oils for food.

6.6.3 Edible and Inedible Fats

In commerce a distinction is commonly made between *edible* and *inedible* fats, based either upon external characteristics, such as unattractive color, taste, or odor, or upon sentimental considerations, such as revolting origin (from garbage, for example), decomposition, or the possibility of contamination with a poisonous substance or with the germs of disease. The distinction between edible and inedible fats is nevertheless a purely practical one, for with modern methods nearly all fats can be refined or modified to the point of physiological edibility. That the distinction exists at all is because it is either unprofitable to convert inedible into edible fat to a greater extent than is done or else because such conversion is not permitted for sanitary reasons.

Sanitary considerations are a more important factor deterring the transformation of inedible into edible fats in the case of animal than in the case of vegetable products, for animal fats may be treated as inedible, even if they are not repulsive to the senses, because their origin is revolting. The degree and effectiveness of such inspections vary in different sections and in different countries.

6.6.4 Drying and Non-drying Oils

In commerce the distinction between edible and inedible fats is not the only one that is made. A different but equally important distinction is drawn between the drying and the non-drying oils. The two kinds of distinction are not comparable, for both non-drying and drying oils may be either edible or inedible. For example, in Europe linseed oil (a typical drying oil) is used for food, whereas in America it is not now so used -- for one reason because it is too expensive as compared with non-drying oils which are readily available in abundance.

Drying oils absorb oxygen from the air and are thereby converted into plastic, elastic, resin-like substances. Hence, when exposed in a thin layer, as in painting, they form a tough, elastic, waterproof film which adheres tightly to the painted surface and protects it from the weather. The two chief drying oils are linseed oil and tung (china wood) oil, which find wide use in the manufacture of paints, varnishes, artificial rubber, linoleums, and other coverings.

The non-drying oils find a wide variety of industrial uses: they enter into soaps and cleansers, cosmetics, lubricants, leather dressings, and candles. They are used in the processes of wool manufacture, especially carding; they are employed in making tin plate and in foundry work. Fats and oils, whether edible or inedible, drying or non-drying, have still other industrial uses. They were the primitive illuminants and are still so used in a relatively slight degree.

6.6.5 Deterioration of Fats and Oils

Fats and oils are quite unstable substances. When stored for any considerable length of time, especially when the temperature is high and the air has free access to them, they deteriorate and spoil. In this respect different fats differ markedly. Some spoil very much more rapidly than others. Among the various fats, spoilage takes the form of rancidity. The fat acquires a peculiarly disagreeable odor and flavor. A vast amount of scientific research has been carried on to determine the cause and nature of rancidity, but investigators are far from agreement on the subject. For present purposes it is sufficient to point out that spoilage of a fat, usually identical with rancidity, is accompanied by partial splitting of the fat into glycerin and fatty acids. The glycerin disappears, or at any rate is unobjectionable, but the fatty acids remain dissolved in the fat, give it an acid reaction, and contribute to its objectionable rancid flavor.

The rancidity of a given parcel of fat is not necessarily the result of long storage under unfavorable conditions. The fat may have been spoiled and rancid from the moment of its production. This will inevitably be true when the materials from which it was produced have undergone decomposition. Thus the fat obtained from putrefying carcasses will be rancid and so will the oil expressed from fermented cottonseed. In other words, to obtain a sound and sweet fat, the raw material must be sound and sweet; it must be worked up speedily before it has had time to decompose; and this must be done under clean and sanitary conditions. The fat thus

obtained must be stored under favorable conditions and its consumption cannot be too long delayed. These conditions it is difficult to obtain in many of the less civilized portions of the world, especially in the tropics, where many fat- and oil-yielding raw materials are produced. Hence fats and oils made at the source of the raw materials may be less sound than those produced at or near the place of consumption.

The fact that so great a proportion of the fat supply, especially vegetable oils, is or becomes rancid and decomposed, necessitates refining, decolorizing, and deodorizing. Certain oils such as cottonseed oil require refining even when they are not decomposed, because they contain certain impurities and are of dark color. The act of refining is not merely an item of expense, but in the case of decomposed fats it involves the removal of the fatty acid contaminating the fat or oil.

6.6.6 Saturated and unsaturated fats

Dear student, from your previous knowledge you know the difference between saturated and unsaturated hydrocarbons, now you learn the difference between saturated and unsaturated fats.

A fat's constituent fatty acids may also differ in the number of hydrogen atoms that are bonded to the chain of carbon atoms. Each carbon atom is typically bonded to two hydrogen atoms. When a fatty acid has this typical arrangement, it is called "**saturated**", because the carbon atoms are saturated with hydrogen; meaning they are bonded to as many hydrogens as possible. In other fats, a carbon atom may instead bond to only one other hydrogen atom, and have a double bond to a neighboring carbon atom. This results in an "unsaturated" fatty acid. More specifically, it would be a monounsaturated fatty acid, whereas, a polyunsaturated fatty acid would be a fatty acid with more than one double bond.

Saturated and unsaturated fats differ in their energy content and melting point. Since an unsaturated fat contains fewer carbon-hydrogen bonds than a saturated fat with the same number of carbon atoms, unsaturated fats will yield slightly less energy during metabolism than saturated fats with the same number of carbon atoms. Saturated fats can stack themselves in a closely packed arrangement, so they can freeze easily and are typically solid at room temperature. But the rigid double bond in an unsaturated fat fundamentally changes the chemistry of the fat.

6.6.7 Trans fatty acids

There are two ways the double bond may be arranged: the isomer with both parts of the chain on the same side of the double bond (the *cis*-isomer), or the isomer with the parts of the chain on opposite sides of the double bond (the *trans*-isomer). Most *trans*-isomer fats (commonly called trans fats) are commercially produced rather than naturally occurring. The *cis*-isomer introduces a kink into the molecule that prevents the fats from stacking efficiently as in the case of fats with saturated chains. This decreases intermolecular forces between the fat molecules, making it more difficult for unsaturated *cis*-fats to freeze; they are typically liquid at room temperature. Trans fats may still stack like saturated fats, and are not as susceptible to metabolization as other fats.

6.7 Analysis of oils and fats

Dear student, you have learnt that processing of animal fats and oils, animal and plant source of oils and fats, edible and nonedible fats, drying and nondrying oils, saturated and unsaturated fats. Now under this main content you learn Analysis of oils and fats. From your previous knowledge can you define the term analysis? Let warm up your self with the following activities.



Learning task 6.7



- a) Why Analysis of fats and oils is carried out
- b) Mention some of the routine tests carried out on fats and oils

Dear student, fats and oils are a heterogeneous group of predominantly hydrophobic compounds. The distinction between fats and oils does not have a chemical basis. Those fats/oils that remain liquid at normal (ambient) temperature are generally taken as oil and those that remain solid, fats.

Analysis of fats and oils is carried out for various reasons, some of the reasons are:

1. Shelf life study (how long the item will remain without deterioration in quality under a given set of conditions)
2. Functional quality (e.g., suitability for use in biscuits, bakery, hydrogenation, etc.)
3. Sensory quality (e.g., rancidity)

4. Nutritional quality (e.g., melting point, polyunsaturated fatty acids)
5. As an aid in controlling production operation (e.g., control of hydrogenation, recovery of oil in mills)
6. Conformance to regulatory standards (e.g., with respect to free fatty acids, saponification value, peroxide value, moisture)
7. Detection of adulteration (e.g., contamination with mineral oil and argemone oil, adulteration of dairy ghee with vegetable ghee)
8. Advanced research (e.g., determination of fatty acid profile)

Some of the routine tests carried out on fats and oils are as follows:

- Acid value/Free fatty acid (FFA)
- Saponification value, SV (also termed Saponification number)
- Iodine value, IV (Also termed Iodine number)
- Unsaponifiable matter
- Refractive index
- Melting point (for solid and semisolid items)
- Moisture content
- General tests for adulteration, such as Hexabromide test for the presence of linseed oil,

For example, Halphen test is used to test for the presence of cottonseed oil, Baudouin test used to test for the presence of vegetable ghee in dairy ghee, Bellier turbidity test used to test for the presence of ground nut oil, etc. Some of the special tests used for particular fats and oils are:

1. Crismer test for rapeseed and mustard oil
2. Reichert-Meissl, Polenske and Kirschner values for dairy ghee
3. Polybromide test for linolenic oils such as linseed oil

6.8. Hydrogenation of oils

Dear student, you have learnt that Analysis of fats and oils is carried out for various reasons. Now under this main content you learn how oils are hydrogenated. What do you understand from the term hydrogenation? Let warm up your self with the following activities.



Learning task 6.8



- a) Define Hydrogenation of oils
- b) Explain why oils are hydrogenated
- c) Mention some of the uses of hydrogenation of oils

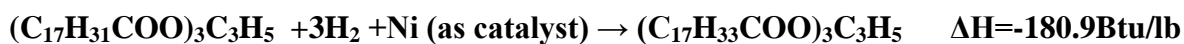
Hydrogenation or hardening as applied to fats and oils might be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of catalyst. This constitutes one of the chief commercial examples of the chemical conversion of hydrogenation. Various fats and oils, such as soybean, cottonseed, fish, whale, and peanut, are converted by partial hydrogenation into fats of a more suitable composition for shortenings, margarine, and edible purposes, as well as for soap making and numerous other industrial uses.

The objective of the hydrogenation is not only to raise the melting point, but greatly to improve the keeping qualities, taste, and odor of many oils. It is frequently accompanied by isomerization, with a significant increase in melting point, caused for example; by oleic (cis) isomerizing to elaidic acid (trans form). The application of the chemical conversion of hydrogenation to oils has been more important and far-reaching than any other chemical improvement in this industry.

6.8.1 Reaction and energy changes

As the reaction itself is exothermic, the chief energy requirements are in the production of hydrogen, hydrogen, warming of the oil, pumping, and filtering:

The reaction may be generalized:



Manufacture of hydrogenated oils consists of hydrogen-generating equipment, catalyst equipment, equipment for refining the oil prior to hydrogenation, a converter for the actual hydrogenation, and equipment for post hydrogenation treatment of the fat. The hydrogen needed may be manufactured by a number of methods, but the hydrocarbon-steam process has mostly replaced the others. The amount of hydrogen necessary is a function of the reduction of unsaturation, as measured by the decrease in the iodine number during hydrogenation.

6.8.2 Interesterification of triglycerides of triglycerides of lard

An advance in fat chemistry which has recently affected the overall ratio of crude fats used in shortening manufacture has been the laboratory perfection and large-scale production of shortening containing lard processed by random and directed interesterification. For many years the blending of lard into good shortening has been blocked by certain undesirable inherent characteristics in the lard.

6.8.3 Isomerization reactions: - In addition to the formation of more saturated compounds during hydrogenation, the reaction may be accompanied by the formation of isomeric unsaturated fatty acids. These may be positional isomers resulting from the migration of double bonds or geometric (spatial) isomers from the conversion of the naturally occurring cis to the trans form. These isomers are of considerable interest, chiefly because of their different physical properties. There is also evidence that the rate of hydrogenation of the different isomers varies, so that their presence would affect the overall reaction rate and final composition.

Generally, it can be summarized as *'the food fat processor can purify to a high degree the natural crude oils'*. She/he can change the character of the side chain fatty acids by hydrogenation, and change their relative positions in the triglyceride randomly or controlled by interesterification.

6.9. Manufacture of soap

Dear student, you have learnt how oils are Hydrogenated, why oils are hydrogenated and uses of hydrogenation of oils. Now under this main content you learn Manufacturing process of soap, the Chemistry of Soap and Detergent Function. Can you explain the manufacturing process of soap and its chemistry? Let warm up your self with the following activities.



Learning task 6.9



- Explain the functional Chemistry of Soaps and Detergents
- Discuss the Soap manufacturing process
- Mention some of the uses of Soap

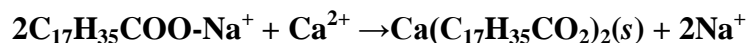
6.9.1 Introduction

Soap is integral to our society today, and we find it hard to imagine a time when people were kept sweet-smelling by the action of perfume rather than soap. However, the current widespread use of soap is only a very recent occurrence, despite the fact that it has been made for more than 2500 years. Early this century the first synthetic detergents were manufactured, and these have now taken the place of soap for many applications.

Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO^-Na^+$. The cleaning action of soap results largely from its emulsifying power and its ability to lower the surface tension of water. This concept may be understood by considering the dual nature of the soap anion. An examination of its structure shows that the stearate ion consists of an ionic carboxyl “head” and a long hydrocarbon

“tail”. In the presence of oils, fats, and other water-insoluble organic materials, the tendency is for the “tail” of the anion to dissolve in the organic matter, whereas the “head” remains in aquatic solution. Thus, the soap emulsifies, or suspends, organic material in water.

The primary disadvantage of soap as a cleaning agent comes from its reaction with divalent cations to form insoluble salts of fatty acids:



These insoluble solids, usually salts of magnesium or calcium, are not at all effective as cleaning agents. In addition, the insoluble “curds” form unsightly deposits on clothing and in washing machines. If sufficient soap is used, all of the divalent cations may be removed by their reaction with soap, and the water containing excess soap will have good cleaning qualities. This is the approach commonly used when soap is employed with hard water (unsoftened water) in the bathtub or wash basin, where the insoluble calcium and magnesium salts can be tolerated.

However, in applications such as washing clothing, the water must be softened by the removal of calcium and magnesium or their complexation by substances such as polyphosphates. Although the formation of insoluble calcium and magnesium salts has resulted in the essential elimination of soap as a cleaning agent for clothing, dishes, and most other materials, it has distinct advantages from the environmental standpoint. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence, any effects that soap might have in solution are eliminated. With eventual biodegradation, the soap is completely eliminated from the environment. Therefore, aside from the occasional formation of unsightly scum, soap does not cause any substantial pollution problems.

6.9.2 The Chemistry of Soap and Detergent Function

All soaps and detergents contain a surfactant as their active ingredient. This is an ionic species consisting of a long, linear, non-polar 'tail' with a cationic or anionic 'head' and a counter ion. The tail is water insoluble and the head is water soluble - a difference in solubility which has two important implications. Firstly, this makes the surfactant molecule a wetting agent: the tails migrate to align themselves with the solid: water interface, lowering the surface tension at that point so that it penetrates the fabric better. Secondly, it allows the oily dirt particles to form an emulsion with the water: the tails of many surfactant molecules surround an oily dirt particle, forming a micelle with a drop of oil in the centre and the ionic heads of the surfactant molecules pointing outwards and hence keeping the micelle in the polar solution.

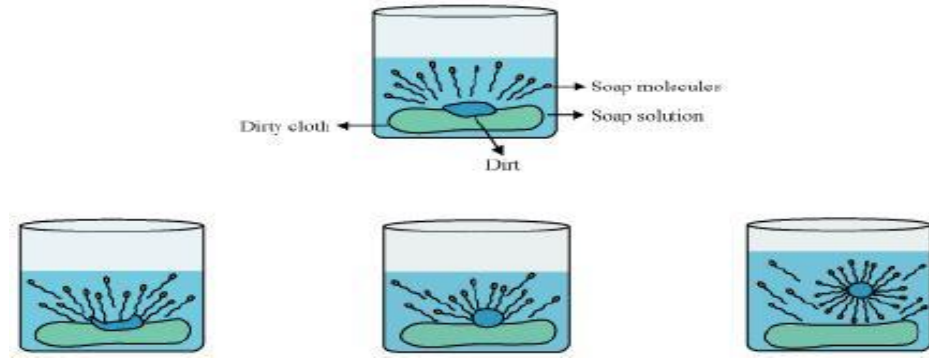


Fig. 6.9.2 Cleansing action of soaps and detergents

6.9.3 The Soap manufacturing process

The essence of soap production is the saponification reaction: a triglyceride caustic soda glycerine metal soap. This reaction is exothermic, and progresses quickly and efficiently at around 125°C inside an autoclave type reactor. The most common fats and oils used are tallow (beef or mutton/beef blend), coconut oil, and palm kernel oil. Different oils produce soaps of varying hardness, odour and lathering, so the ratios of the oils used are closely monitored to produce a blend with the most desirable characteristics for the most reasonable cost.

However, pure soap is hard and easily oxidised, so various additives are added to correct this and to make a more aesthetically pleasing product. The first such "additive" is glycerine, which is produced in the saponification reaction. Glycerine makes the soap smoother and softer than pure soap. However, it is also much more valuable than soap itself, so only a minimum of glycerine is left in the soap and the remainder is extracted, purified and sold.

The glycerine is extracted from the soap with a brine solution that is added to the soap at the saponification stage. Wet soap is soluble in weak brine, but separates out as the electrolyte concentration increases. Glycerine, on the other hand, is highly soluble in brine. Wet soap thus has quite a low electrolyte concentration and is about 30% water (which makes it easily pumpable at 70°C). To remove the glycerine, more electrolytes are added, causing the wet soap to separate into two layers: crude soap and a brine/glycerine mixture known as spent lye, neutral lye or sweet waters.

The soap still contains some salt, which itself functions as an additive, altering the viscosity and colour of the soap. Once the spent brine solution has been removed the soap is dried, chipped,

mixed with other additives such as perfumes and preservatives and then plodded (squeezed together), formed into tablets and packaged for sale. Soap is produced industrially in *four basic steps*.

Step 1 - Saponification

A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and heated. The soap produced is the salt of a long chain carboxylic acid.

Step 2 - Glycerine removal

Glycerine is more valuable than soap, so most of it is removed. Some is left in the soap to help make it soft and smooth. Soap is not very soluble in salt water, whereas glycerine is, therefore, salt is added to the wet soap causing it to separate out into soap and glycerine in salt water.

Step 3 - Soap purification

Any remaining sodium hydroxide is neutralized with a weak acid such as citric acid and two thirds of the remaining water removed.

Step 4 - Finishing

Additives such as preservatives, color and perfume are added and mixed in with the soap and it is shaped into bars for sale. Detergents are similar in structure and function to soap, and for most uses they are more efficient than soap and so are more commonly used. In addition to the actual 'detergent' molecule, detergents usually incorporate a variety of other ingredients that act as water softeners, free-flowing agents etc.

6.10 Introduction to Detergents

Dear student, you have learnt that Manufacturing process of soap, the Chemistry of Soap and Detergent Function of soap. Now under this main content you learn Manufacturing process of detergents, byproducts of detergents, how we can control the quality of detergents, and environmental aspects of detergents. Can you explain what detergents are? Let warm up your self with the following activities.



Learning task 6.10



- a) Explain the Chemistry of Detergents
- b) Discuss the manufacturing process of detergents
- c) Explain the difference among laundry detergents to other types of detergents
- d) Discuss how quality of detergents is monitored
- e) Mention some of the uses of detergents

6.10.1 Manufacturing of Detergents

Synthetic **detergents** have good cleaning properties and do not form insoluble salts with “hardness ions” such as calcium and magnesium. Such synthetic detergents have the additional advantage of being the salts of relatively strong acids and, therefore, they do not precipitate out of acidic waters as insoluble acids, an undesirable characteristic of soaps. The potential of detergents to contaminate water is high because of their heavy use throughout the consumer, institutional, and industrial markets.

Most of this material, along with the other ingredients associated with detergent formulations, is discarded with wastewater.

The key ingredient of detergents is the **surfactant** or surface-active agent, which acts in effect to make water “wetter” and a better cleaning agent. Surfactants concentrate at interfaces of water with gases (air), solids (dirt), and immiscible liquids (oil). They do so because of their **amphiphilic structure**, meaning that one part of the molecule is a polar or ionic group (head) with a strong affinity for water, and the other part is a hydrocarbon group (tail) with an aversion

to water. This kind of structure is illustrated below for the structure of alkyl benzene sulfonate (ABS) surfactant:

Until the early 1960s, alkyl benzene sulfonate ABS was the most common surfactant used in detergent formulations. However, it suffered the distinct disadvantage of being only very slowly biodegradable because of its branched-chain structure. The most objectionable manifestation of the nonbiodegradable detergents, insofar as the average citizen was concerned, was the “head” of foam that began to appear in glasses of drinking water in areas where sewage was recycled through the domestic water supply.

Consequently, ABS was replaced by a biodegradable surfactant known as linear alkyl sulfonate LAS. LAS, α -benzenesulfonate, has the general structure illustrated at the top of the next page where the benzene ring may be attached at any point on the alkyl chain except at the ends. LAS is more biodegradable than ABS because the alkyl portion of LAS is not branched and does not contain the tertiary carbon which is so detrimental to biodegradability. Since LAS has replaced ABS in detergents, the problems arising from the surface-active agent in the detergents (such as toxicity to fish fingerlings) have greatly diminished and the levels of surface-active agents found in water have decreased markedly.

Other ingredients include ion exchangers, alkalies (sodium carbonate), anticorrosive sodium silicates, amide foam stabilizers, soil-suspending carboxymethylcellulose, bleaches, fabric softeners, enzymes, optical brighteners, fragrances, dyes, and diluent sodium sulfate. Of these materials, the polyphosphates have caused the most concern as environmental pollutants, although these problems have largely been resolved. Increasing demands on the performance of detergents have led to a growing use of enzymes in detergent formulations destined for both domestic and commercial applications. To a degree, enzymes can take the place of chlorine and phosphates, both of which can have detrimental environmental consequences. Lipases and cellulases are the most useful enzymes for detergent applications.

Detergents use a synthetic surfactant in place of the metal fatty acid salts used in soaps. They are made both in powder and liquid form, and sold as laundry powders, hard surface cleansers,

dish washing liquids, fabric conditioners etc. Most detergents have soap in their mixture of ingredients, but it usually functions more as a foam depressant than as a surfactant. Liquid detergents were introduced that utilized sodium citrate and sodium silicate. The liquids offered superior performance and solubility at a slightly increased cost. Some current trends, including the introduction of superconcentrated powder detergents, will probably lead to an increase in spray drying operations at some facilities. Manufacturers are also developing more biodegradable surfactants from natural oils.

6.10.2 Quality Control in manufacturing of detergents

Manufacturers constantly monitor the quality of their detergents, and they utilize the same testing methods to assess the effectiveness of new products. In one method, light is shined onto a piece of fabric that has been soiled and then washed in the test detergent. To make liquid detergent, the dry powder is simply mixed back in with a solution consisting of water and chemicals known as "solubilizers." These chemicals help the water and detergent blend together more evenly.

Another method involves laboratory burning of a small amount of material that has been soiled and then laundered. The weight of the ashes, plus the weight of the gaseous results of the burning, reveals how much of the dirt remained in the fabric after laundering. A result that is much higher than a clean test sample indicates that a significant amount of dirt was retained in the laundered sample. Naturally, the goal is to come as close to the weight of a clean control sample as possible.

6.10.3 Byproducts in manufacturing of detergents

In recent years, the laundry detergent industry has been faced with two environmental challenges, both of which have seemed to have been dealt with successfully. Environmentalists were concerned that phosphate builders added large amounts of phosphorous compounds to the nation's waterways. Acting as a fertilizer, the phosphorus stimulated the growth of algae, and these unnaturally large crops of algae significantly depleted the amount of dissolved oxygen in water. This decrease in free oxygen harmed other marine life, thus threatening to disrupt normal ecological patterns.

This problem, and the environmental pressure and legislation prompted in the late 1960s, led manufacturers to develop effective builders that did not contain phosphates. Today, detergents sold in many states are phosphate-free. Although this adjustment did not entail a change in the manufacturing process, it did require a research effort that took several months to devise a satisfactory alternative.

6.10.4 Environmental Implications of detergents

Soap is designed as a product to be used once then flushed down the drain, so as expected the environmental implications of its manufacture are not nearly so great as many other chemical processes. There are two main areas of concern: the safe transport and containment of the raw materials and the minimization of losses during manufacture. The three main components of soap by both cost and volume are oils, caustic and perfumes.

Oils and perfume are immiscible in water and if spilled create havoc, although the oils do solidify at room temperature. Transport of these products is by trained carriers, and the systems for pumping from the truck to storage tanks are carefully designed. Hence the losses in the plant will indirectly be minimized because the process itself is being monitored. There has recently been a strong move away from the environmentally hazardous biologically stable detergents used in the past to biodegradable ones.



Chapter Summary



- Fats and oils are found widely distributed in nature, in both the plant and the animal kingdoms. The fats and oils have always had an essential role as food for mankind
- The common physical properties of oils and fats are: they float on water but are not soluble in it; they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue, i.e., ash.
- The common chemical characteristic of oils and fats are capable of serving as foodstuffs may be decomposed into glycerin and one or more acids of the class known to chemists as fatty acids.
- Animal fats and oils are derived both from terrestrial and marine animals. Marine fats include liver oils, blubber oils, and fish oils.
- Vegetable fats and oils are found in greatest abundance in fruits and seeds. While fats and oils do occur in the roots, stalks, branches, and leaves of plants, they are rarely present in these organs in quantities large enough for commercial purposes.
- The vegetable oil processing industry involves the extraction and processing of oils and fats from vegetable sources.
- Vegetable fats and oils are principally used for human consumption but are also used in animal feed, for medicinal purposes, and for certain technical applications.
- The overall processing of crude vegetable oils usually involves alkali refining, water washing and drying, bleaching, hydrogenation, and deodorizing.
- For both animal and vegetable oils contain processing steps in common, e.g., refining, bleaching, hydrogenating, and deodorizing.
- Hydrogenation or hardening as applied to fats and oils might be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of catalyst.

- The objective of the hydrogenation is not only to raise the melting point, but greatly to improve the keeping qualities, taste, and odor of many oils.
- Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO^-Na^+$. The cleaning action of soap results largely from its emulsifying power and its ability to lower the surface tension of water.
- All soaps and detergents contain a surfactant as their active ingredient. This is an ionic species consisting of a long, linear, non-polar 'tail' with a cationic or anionic 'head' and a counter ion. ***The tail is water insoluble and the head is water soluble***
- Synthetic detergents have good cleaning properties and do not form insoluble salts with "hardness ions" such as calcium and magnesium.
- The key ingredient of detergents is the surfactant or surface-active agent, which acts in effect to make water "wetter" and a better cleaning agent. Surfactants concentrate at interfaces of water with gases (air), solids (dirt), and immiscible liquids (oil).



Self test exercises



1. Explain the chemistry of fats and oils
2. Compare and contrast fats and oils
3. Compare and contrast vegetable oils, animals' oils and fats, and waxes
4. Explain how vegetable oils are manufactured industrially
5. Explain the advantage of analyzing fats and oils
6. Discuss why oils are hydrogenated
7. Soap and detergents are some of essential products in our day today activity
 - a) Explain the Chemistry of Soap and Detergent Function
 - b) Discuss the manufacturing process of Soap
 - c) Explain the difference among laundry detergents to other types of detergents



Unit Introduction

Dear student, this chapter deals with Pulp and Paper Industry. We will also discuss further about Manufacture of pulp, Refining of pulp and Manufacture of paper.



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Explain the basic principle in the manufacturing process of the pulp and paper industry
- List the main raw materials in pulp and paper industry
- Discuss how a pulp is refined and processed
- Explain the use of bleaching in paper industry

7.1 Introduction

Dear student, Paper is the most important material that is used in our day to day activity. From your experience mention some of the uses of paper, Let warm up your self with the following



Learning task 7.1



- a) Explain the history of pulp and paper industry
- b) List the main raw materials in pulp and paper industry

The pulp and paper industry has been consuming much energy and water ever since Cailun (an inventor of paper in ancient China) invented paper in A.D. 105. He crushed the bark of the shrub with a stone mill to extract fibers, and separated the single fibers by washing them in water. When they were uniformly distributed underwater, they were dewatered and formed by a drain board. Then the wet paper was dried in the sun for a long time, and final paper products were obtained.

The basic principle in the manufacturing process of the pulp and paper industry today has undergone almost no change, but industry has developed into a process industry constituting the continuous production processes. The pulp and paper industry is also noted for a great percentage of the energy cost in the total production cost. The industry is continuously evolving to meet the demand for products that are manufactured cleanly, efficiently, and cost-effectively from wood.

The industry is composed of paper and/or paperboard mills, pulp mills, and integrated pulp and paper mills. Integrated mills are generally larger and more cost-effective than nonintegrated mills, but the smaller size of the nonintegrated mills allows them to be located closer to the consumer. The percentage of integrated mills has fallen slightly distributed and this downward trend could continue. Pulp and paper mills are highly complex and integrate many different process areas including:

- wood preparation,
- pulping,
- chemical recovery,
- bleaching, and
- Papermaking to convert wood to the final product Processing options and the type of wood processed are often determined by the final product.

The main raw materials that are used for papermaking are:

- Pulpwood (trees);
- Recovered paper or paperboard products; and
- Non wood plant sources such as cotton, sugarcane bagasse, and bamboo.

7.2 Manufacture of pulp

Dear student, you have learnt that the history of paper and pulp industry, the main raw materials for pulp and paper. Now, you learn how pulp is manufactured. Do you know what pulp means?

Let warm up your self with the following activities.



Learning task 7.2



- a) Discuss the major pulping Processes
- b) Compare and contrast the common pulping process

Pulping is the process of reducing wood (or other cellulosic fiber source) into a fibrous mass suitable for papermaking. The process of pulping involves breaking the chemical bonds of the raw material through mechanical and/or chemical means in order to liberate the discrete fibers used to make paper. Once the fibers are separated, they are screened, washed to varying degrees, thickened, and sent to pulp storage.

7.2.1 Pulping Processes

The particular pulping process used affects the strength, appearance, and intended use characteristics of the resultant paper product. Pulping is the major source of environmental impacts in the pulp and paper industry. Commercial pulping operations are broadly grouped into four categories: **chemical, semi chemical, mechanical, and recycled.**

7.2.1.1 Mechanical Pulping

Mechanical pulping separates wood fibers using vibrational forces. In mechanical pulping processes, wood in the form of small logs or chips is converted into fibers by mechanical action. Repeated compression and decompression of the wood in the grinder or refiner causes the fibers to weaken, fatigue, and separate. Pressure, heat, and chemicals may also be added to aid in softening the lignin that binds the fibers together. The different types of mechanical pulping are classified by the type of refining action used and whether pressure, steam, or chemicals are used to make the pulp. Mechanical pulping is electricity-intensive, with the electricity demands varying depending on the desired pulp qualities.

7.2.1.2 Thermo mechanical pulping

Thermo mechanical pulp is a pulp produced by processing wood chips using heat (thermo) and a mechanical refining movement (mechanical). It is a two stage process where the logs are first stripped of their bark and converted into small chips. These chips have a moisture content of around 25-30% and a mechanical force is applied to the wood chips in a crushing or grinding action which generates heat and water vapour and softens the lignin thus separating the individual fibres. The pulp is then screened and cleaned; any clumps of fibre are reprocessed. This process gives a high yield of fibre from the timber and as the lignin has not been removed,

the fibres are hard and rigid. Thermomechanical pulping (TMP) is the most energy-intensive pulping process,

7.2.1.3 Mechanical and thermochemical pulping (*Chemithermomechanical pulping*)

Wood chips can be pretreated with sodium carbonate, sodium hydroxide, sodium sulfite and other chemicals prior to refining with equipment similar to a mechanical mill. The conditions of the chemical treatment are much less vigorous (lower temperature, shorter time, less extreme pH) than in a chemical pulping process since the goal is to make the fibres easier to refine, not to remove lignin as in a fully chemical process. Pulps made using these hybrid processes are known as chemithermomechanical pulps (CTMP).

7.2.1.4 Chemical Pulping

Chemical pulping is the dominant pulping process used for papermaking today, mainly because it can produce a strong pulp from a wide variety of tree species. Chemical pulping dissolves Lignin and other Non-Cellulose Components. Compared with mechanical and semi chemical pulps, chemical pulp fibers have higher strength properties, greater resistance to aging, and are more easily bleached. In addition, the kraft process utilizes an efficient chemical recovery system that generates a significant portion of the energy required for pulping.

The major disadvantages associated with chemical pulping are lower yield, high capital cost of the equipment, and objectionable odors produced by the sulfurous compounds used in the process. Chemical pulping processes cook wood chips at elevated temperature and pressure with chemicals to dissolve the noncellulose components (primarily lignin) and separate the fibers. Because the process dissolves some of the cellulose and hemicellulose fibers along with the lignin, the overall pulp yield is relatively low. The two major chemical processes are the *kraft (sulfate) process* and the *sulfite process*.

Chemical method for producing wood pulp using caustic soda and sodium sulfide as the liquor in which the pulpwood is cooked to loosen the fibres. The process (from German *kraft*, "strong") produces particularly strong and durable paper; another advantage is its capability of digesting pine chips; resins dissolve in the alkaline liquor and are recovered as tall oil, a valuable by-

product. Recovery of sodium compounds is important in the economy of the process. In modern kraft mills, operations are completely contained; waste streams are recycled and reused, eliminating water pollution.

7.2.1.5 Kraft (Sulfate) Pulping

Wood chip feedstock is cooked in steam heated digesters with an alkaline “white liquor” mixture containing mainly sodium hydroxide (NaOH) and sodium sulfide (Na₂S) and weak black liquor from a preceding cook as makeup. Cooking time and temperature depend on a number of variables, including fiber source and the degree of delignification required. Digestion may be either batch or continuous. Batch digesters have lower capital costs and offer more product flexibility.

7.2.1.6 Recycled Paper Pulping

In recycled fiber pulping, the recovered paper is loaded into a vat where the *secondary fibers are re-hydrated* and dispersed in slurry. Recovered paper recycling systems typically include processes for repulping, contaminant removal, screening, and bleaching. Processes that produce newsprint, tissue or other “bright” grades also include a deinking step, which requires the addition of chemicals during pulping. **Recycled pulp** is also called **deinked pulp (DIP)**.

Deinked pulp (DIP) is recycled paper which has been processed by chemicals, thus removing printing inks and other unwanted elements and freed the paper fibers. The process is called deinking. DIP is used as raw material in papermaking. Many newsprint, toilet paper and facial tissue grades commonly contain 100% deinked pulp and in many other grades, such as lightweight coated for offset and printing and writing papers for office and home use, DIP makes up a substantial proportion of the furnish.

7.2.1.7 Alternative pulping methods

Research is under way to develop biological pulping, similar to chemical pulping but using certain species of fungi that are able to break down the unwanted lignin, but not the cellulose fibres. This could have major environmental benefits in reducing the pollution associated with chemical pulping. The pulp is bleached using chlorine dioxide stage followed by neutralization

and calcium hypochlorite. The oxidizing agent in either case oxidizes and destroys the dyes formed from the tannins of the wood and accentuated (reinforced) by sulfides present in it.

7.2.1.8 Effluents from pulp mills

The process effluents are treated in a biological effluent treatment plant, which guarantees that the effluents are not toxic in the recipient. Mechanical pulp is not a major cause for environmental concern since most of the organic material is retained in the pulp, and the chemicals used (hydrogen peroxide and sodium dithionite) produce benign byproducts (water and sodium sulfate (finally), respectively). Chemical pulp mills, especially Kraft mills, are energy self-sufficient and very nearly closed cycle with respect to inorganic chemicals. Bleaching with chlorine produces large amounts of organochlorine compounds, including dioxins.

7.3 Bleaching of pulp

Dear student, you have learnt the various methods that are used for Manufacture of pulp. Under this main content you learn bleaching. What do know from the term bleaching? Let warm up your self with the following activities.



Learning task 7.3



- a) Explain whether bleaching is a physical or chemical process
- b) Discuss the use of bleaching in pulp and paper industry

Bleaching is a chemical process that is used to whiten and brightens Pulp. The pulp produced in the process can be bleached to produce a white paper product. However, the chemicals used to bleach pulp have been a source of environmental concern, and recently the pulp industry has been using alternatives to chlorine, such as:

- Chlorine dioxide,
- Oxygen,
- Ozone and
- Hydrogen peroxide.

Unbleached pulps from the various pulping processes are brown or crème in color due to light absorbing compounds contained in the lignin that were not removed from the pulp during the pulping process. Therefore, before the pulp can be converted to paper products, it must be subjected to a chemical bleaching process to whiten or brighten the pulp.

7.4 Manufacture of Paper

Dear student, you have learnt Bleaching is a chemical process that is used to whiten and brightens Pulp. Under this main content you learn manufacture of Paper. Can you explain the major manufacturing process of paper? Let warm up your self with the following activities.



Learning task 7.4



- a) Explain manufacturing process of paper
- b) Discuss the use of additives in the manufacturing process of paper
- c) Discuss the source of pollutants in paper industry

Dear student, Paper making operations are divided into two sections - *“wet end” and “dry end”*. It begins with the preparation of homogeneous pulp slurry (stock), where various chemicals and mineral additives may be added to achieve the desired final product. The slurry is then fed into the papermaking machine, where it is formed into a sheet and subsequently subjected to pressing and drying operations. The dry sheets are collected on reels for off-machine finishing operations. Further surface treatments may be necessary, depending on the intended end use of the paper

7.4.1 Additives

Besides the fibers, pulps may contain fillers such as chalk or china clay, which improve the characteristics of the paper for printing or writing. Additives for sizing purposes may be mixed into the pulp and/or applied to the paper web later in the manufacturing process. The purpose of sizing is to establish the correct level of surface absorbency to suit the ink or paint.

7.4.2 Pollution control: Environmental Overview

Dear student as you have learnt pulp and paper making requires large inputs of water, energy, chemicals, and wood resources, and produces various wastes and emissions that must be controlled or treated. Impacts on the environment can potentially come from toxic and hazardous chemicals in air and water emissions, thermal loading to natural waterways, odor-causing chemicals, air pollutants from combustion, and solid wastes.

The industry is taking steps to minimize environmental impacts by increasing the use of recycled paper, improving energy efficiency, and making capital investments for effective compliance with regulations. Pulp and papermaking processes have traditionally consumed large amounts of water, generating wastewater that can contain chlorinated compounds, volatile organics, sulfur compounds, and other chemicals. Now days, mills are implementing technologies that reduce process water requirements, and must ensure that effluents released to waterways or to publicly-owned treatment works (POTWs) meet the guidelines established by the U.S. Environmental Protection Agency (EPA).



Chapter summary



- The basic principle in the manufacturing process of the pulp and paper industry today has undergone almost no change, but industry has developed into a process industry constituting the continuous production processes.
- The main raw materials that are used for papermaking are:
 - ✓ Pulpwood (trees);
 - ✓ Recovered paper or paperboard products; and
 - ✓ Non wood plant sources such as cotton, sugarcane bagasse, and bamboo.
- **Pulping** is the process of reducing wood (or other cellulosic fiber source) into a fibrous mass suitable for papermaking.
- The process of pulping involves breaking the chemical bonds of the raw material through mechanical and/or chemical means in order to liberate the discrete fibers used to make paper.
- Bleaching is a chemical process that is used to whiten and brightens Pulp. The pulp produced in the process can be bleached to produce a white paper product
- Pulp and paper industry can cause impacts on the environment. It can potentially come from toxic and hazardous chemicals in air and water emissions, thermal loading to natural waterways, odor-causing chemicals, air pollutants from combustion, and solid wastes



Self test exercises



1. List the main raw materials in pulp and paper industry
2. Compare and contrast the common pulping process
3. Explain whether bleaching is a physical or chemical process and discuss the use of bleaching in pulp and paper industry
4. The pulp and paper industry has been consuming much energy and water
 - a) Explain the manufacturing process of paper
 - b) Discuss the use of additives for manufacturing process of paper
 - c) Discuss the source of pollutants in paper industry



Unit Introduction

Dear student, this chapter deals with chemical food stuff processing. We will also discuss further about fermentation, Alcohol Beverages, Manufacture of Beer, Spirit and wines and Soft Drink Industry



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Explain the use of fermentation in chemical food stuff processing
- Mention some of Alcohol Beverages
- List the main raw materials used for manufacture of Beer, Spirit and wines
- Compare and contrast the alcoholic content of fermented beverages and distilled sprit
- Mention the manufacturing process of soft drink industry
- Compare and contrast Alcohol Beverages and soft drink industry

8.1. Introduction to fermentation

Dear student, Chemical food stuff processing is a processing that involves the manufacturing of chemical food stuff such as alcoholic beverage, soft drinks, and etc. For the processing of any chemical food stuff fermentation is important. Now you learn what fermentation is, its uses in food processing. Can you define the term fermentation?,Let warm up your self with the following activities.



Learning task 8.1



- a) Define fermentation
- b) Explain the major uses of fermentation

Dear student, the foundation of the scientific understanding of fermentation, indeed of the action of all organisms, and hence of their economic control, rests firmly upon the genius of one man, **Louis Pasteur**. He showed that fermentation is directly caused by the life processes of minute organisms.

Fermentation in food processing typically is the conversion of carbohydrates to alcohols and carbon dioxide or organic acids using yeasts, bacteria, or a combination thereof, under anaerobic conditions. Yeasts and bacteria are unicellular and of very small dimensions. A more restricted definition of fermentation is the chemical conversion of sugars into ethanol. The science of fermentation is known as zymurgy.

Fermentation usually implies that the action of microorganisms is desirable, and the process is used to produce alcoholic beverages such as beer, spirits and wine. Fermentation is also employed in the leavening of bread, and for preservation techniques to create lactic acid in sour foods such as dry sausages, yogurt, or vinegar (acetic acid) for use in pickling foods.

Fermentation may refer to:

- Food Fermentation, the use of fermentation in food preparation
- Fermentation (biochemistry), a metabolic process whereby electrons released from nutrients are ultimately transferred to molecules obtained from the breakdown of those same nutrients
- Brewing Fermenting, the process of fermentation used in brewing beer
- Ethanol fermentation, the production of ethanol for use in food, alcoholic beverage, fuel and industry
- Industrial fermentation, the breakdown and re-assembly of biochemicals for industry, often in aerobic growth conditions
- Tea processing, the term used in the tea industry for the aerobic treatment of tea leaves to break down certain unwanted chemicals and modify others to develop the flavor of the tea.

Fermentation occurs in large fermenting vessels and typically lasts for from one to three days. Some vessels are sealed, recirculating the carbon dioxide. Others, normally in smaller plants, vent to atmosphere via a water trap. The yeast strain used for fermentation depends on the

beverage. The specific gravity of the fermenting mixture is measured regularly as an indication of the sugar content and thereby the degree of fermentation.

- Temperature controls may need to be used as most fermentation will only take place at 5-30°C.
- Many of the chemical reactions caused by microorganisms are very complex, however, and cannot easily be classified; so the concept of fermentation itself as a chemical conversion has been developed.

According to Silox and Lee, the five basic prerequisites of a good fermentation process are:

1. A microorganism that forms a desired end product. This organism must be readily propagated and be capable of maintaining biological uniformity, thereby giving predictable yields
2. Economic raw materials for the substrate, e.g., starch or one of several sugars
3. Acceptable yields
4. Rapid fermentation
5. A product that is readily recovered and purified

According to Lee, certain factors should be stressed in relation to the fermentation chemical-conversion or unit-process concept, such as microorganisms, equipment, and the fermentation itself. Certain critical factors of the fermentation are:

1. the pH,
2. temperature,
3. aeration, agitation,
4. pure-culture fermentation,
5. and uniformity of yields.

The microorganisms should be those which flourish under comparatively simple and workable modifications of environmental conditions.

8.1.1 Uses of fermentation

Fermentation has various benefits. The primary benefit of fermentation is the conversion of sugars and other carbohydrates, e.g., converting juice into wine, grains into beer, carbohydrates into carbon dioxide to leaven bread, and sugars in vegetables into preservative organic acids.

For example; Food fermentation has been said to serve five main purposes:

1. Enrichment of the diet through development of a diversity of flavors, aromas, and textures in food substrates
2. Preservation of substantial amounts of food through lactic acid, alcohol, acetic acid and alkaline fermentations
3. Biological enrichment of food substrates with protein, essential amino acids, essential fatty acids, and vitamins
4. Elimination of anti-nutrients
5. A decrease in cooking times and fuel requirements

8.2 Alcoholic Beverages

Dear student, you have learnt fermentation, its uses for processing of chemical foods. Under this main content you learn Alcoholic Beverages. From your previous knowledge can you explain what beverages are? Let warm up your self with the following activities.



Learning task 8.2



- a) Mention some of Alcohol Beverages
- b) List the main raw materials used for manufacture of Beer, Spirit and wines
- c) Compare and contrast the alcoholic content of fermented beverages and distilled sprit

An alcoholic beverage is a drink containing ethanol. Ethanol is a psychoactive drug, a depressant, and many societies regulate or restrict its sale and consumption. Countries place various legal restrictions on the sale of alcoholic drinks to young people. The consumption of alcohol is often important at social events in such societies and may be an important aspect of a community's culture.

The concentration of alcohol in a drink may be specified in percent alcohol by volume (ABV), in percentage by weight (sometimes abbreviated w/w for weight for weight), and etc. Most yeast cannot grow when the concentration of alcohol is higher than about 18% by volume, so that is a practical limit for the strength of fermented beverages such as wine, beer, and sake. Strains of yeast have been developed that can survive in solutions of up to 25% alcohol by volume, but these were bred for ethanol fuel production, not beverage production.

8.3 Manufacture of Beer, wines and distilled Spirit

Dear student, you have learnt that, an alcoholic beverage is a drink containing ethanol. Under this main content you learn how Beer, wines and distilled Spirit are manufactured industrially.

Can you explain the basic difference between fermented beverages and distilled beverages? Let warm up your self with the following activities.



Learning task 8.3



- a) List the main raw materials used for manufacture of Beer, Spirit and wines
- b) Compare and contrast the alcoholic content of fermented beverages and distilled spirit

8.3.1 Introduction

The making of fermented beverages was discovered by primitive man, and has been practiced as an art for thousand of years. Within the past century and a half this has evolved into a highly developed science.

There are different the basic raw materials that can be used for manufacture of Beer, wine and distilled Spirit. Grains and fruits supplying carbohydrates are the basic raw materials .The variety of grains and fruits employed are wide, changing from country to country or from beverage to beverage. For example, Russia ferments potatoes and by distillation obtains vodka; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, together with the grape.

8.3.2 Manufacture of Beer

Dear student, Beer and allied products are beverages of low alcoholic content (4 to 8%) made by brewing various cereals with hops, usually added to impart a more or less bitter taste and to control the fermentation that follows. The cereals employed are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts.

Brewing sugars and syrups (corn sugar, or glucose) and yeast complete the raw materials. For beer most important cereal is barley, which is converted into mail by partial germination. Beer is also made by the process of fermentation. A liquid mix, called wort, is prepared by combining

yeast and malted cereal, such as corn, rye, wheat or barely. Fermentation of this liquid mix produces alcohol and carbon dioxide. The process of fermentation is stopped before it is completed to limit the alcohol content. The alcohol so produced is called beer. It contains 4 to 8 percent of alcohol.

Brewing is the production of alcoholic beverages and alcohol fuel through fermentation. This is the method used in beer production. Brewing is fundamentally a natural process. The art and science of brewing lies in converting natural food materials into a pure,pleasing beverage. Although great progress have been made with the techniques for achieving high-quality production, beer today is still a beverage brewed from natural products in a traditional way. Although the main ingredients of beer have remained constant (*water, yeast, malt and hops*), it is the precise recipe and timing of the brew that gives one a different taste from another.

8.3.3 Manufacture of Wine

Dear student, Wine has been made for several thousand years by fermentation of the juice of the grape. Like other fermentations, many of the primitive procedures have been supplanted by improved science and engineering, to reduce costs and to make more uniform products. But now, as always, the quality of the product is largely related to grape, soil, and sun, resulting in variation in flavor and aroma. The color depends largely upon the nature of the grapes and whether the skins are pressed out before fermentation.

Wines are classified as natural (alcohol 10 to 22%), fortified (alcohol 14 to 30%), sweet or dry, still or sparkling. For example, for the manufacture of dry red wine, red or black grapes are necessary. Wines are made from a variety of fruits, such as grapes, peaches, or plums. However, the most common wines are produced from grapes. The soil in which the grapes are grown and the weather conditions in the growing season determine the quality and taste of the grapes which in turn affects the taste and quality of wines.

For example, when ripe, the grapes are crushed and fermented in large vats to produce wine. Treatment in wine manufacturing gives a more stable finished wine. By quick-aging methods it is possible to put out a good sweet wine in 4 months. These methods include pasteurization,

refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine may be held at about freezing for 3 weeks to month, and a small amount of oxygen gas bubbled in. Then the wine is racked, clarified, and further filtered in the usual manner.

8.3.4 Distilled spirits

Dear student, various fermented products, upon distillation and aging, yield the distilled liquors. For example, Brandy is distilled from wine or from the marc, which is the pulp left by racking or straining. By making a beer from a grain mixture containing at least 51% of corn and distilling and aging it, bourbon whisky is yielded. Similarly, rye whisky must have started with 51% of rye in the grain to be mashed and fermented. By law, whisky must be fermented from whole grains, so that the germs(containing the corn oil) and the husks are in suspension in the liquor from the beer still in whisky manufacture.

For example, Whisky is made by distilling the fermented juice of cereal grains such as corn, rye or barley. Scotch whisky was originally made in Scotland. The word "Scotch" has become almost synonymous with whisky of good quality. Rum is a distilled beverage made from fermented molasses or sugarcane juice and is aged for at least three years. Caramel is sometimes used for coloring. Whisky, Brandy, Rum, Gin, and Vodka are some common examples of distilled spirits.

Table 8.1 Types of alcoholic beverages and their alcohol content

Beverage	Source	Alcohol content (percentage)
Beer	Cereals	4 - 8
Wines (Port, Sherry, Champagne, etc)	Grapes(also other fruits)	10-22
Brandy	Fruit juices	40 - 50
Whisky	Cereal grains	40 - 55
Rum	Molasses/sugarcane	40 - 55

8.3.5 Environmental aspect of Breweries

The primary sources of pollution from the Beer industries are residue (draft), chemicals and water use. Wastewater discharges are of most concern from an environmental perspective.

8.3.5.1 Solid Waste

Residue is a type of waste called 'draft' which is a residual substance from the beer production process. If this residue is not treated or disposed of, it can become a source of odors. Consequently, the draft is collected daily and removed from the factory site. Broken bottles create a solid waste problem.

8.3.5.2 Air Pollution

Air pollution from plant originates mainly from chemical evaporation, primarily NaOH used in the bottle washing process. Other source of air pollution is emissions from the factory's oil burning boilers. Although both the chemical and boiler emissions are released untreated to the atmosphere, the impact on air is considered negligible and is considered unlikely to affect either the health of factory workers or local area residents.

8.3.5.3 Wastewater

Wastewater is generated during all stages of beer production at the factory. The highest wastewater volumes are generated during:

- Bottle washing
- Spills during bottling
- Floor washing
- Process discharges and tank washing including the cooker, mash tub, and kettle
- Sanitary wastewater

The primary contaminants in the factory's combined wastewater are yeast and worth.

- Other common contaminants are:
 - NaOH used for bottle washing
 - H_3PO_4 used for washing beer tanks
 - Acetic acid, used for killing germs at all stages of production
 - Hypochlorite 60% Cl_2 used for killing germs in raw water
 - Chemicals used for washing floors,
 - Oil and grease used for machinery maintenance

8.4 Soft Drink Industry

Dear student, you have learnt about Alcoholic Beverages such as Beer, wines and distilled Spirit; Under this main content you learn about Soft Drink Industry. Can you mention some of the common soft drinks that are available in the market? Let warm up your self with the following activities.



Learning task 8.4



- a) Explain the difference between alcoholic drink and soft drink industry
- b) Mention the main raw materials for soft drink industry
- c) Discuss the production process of soft drink
- d) Mention some of the main raw materials for soft drink industry

A soft drink (also referred to as soda, soda pop, pop, tonic, coke, or fizzy drink) is a non-alcoholic beverage typically containing water; often carbonated water; and a flavoring agent. Many of these beverages are sweetened by the addition of sugar or high-fructose corn syrup, or in the case of “diet” drinks; with a sugar substitute. They may also contain ingredients such as caffeine and fruit juice. They are called "soft" in contrast to "hard drinks"; that is, alcoholic beverages.

Small amounts of alcohol may be present in a soft drink, but the alcohol content generally must be less than 0.5% of the total volume if the drink is to be considered non-alcoholic. Widely sold soft drink varieties/flavors include cola, lemon-lime, root beer, orange, grape, cream soda, ginger ale, flavored water, tonic water, sparkling lemonade, sparkling water, iced tea, sweet tea, squash, and fruit punch.

Soft drinks are usually served chilled or at room temperature, are rarely heated, and generally do not include milk or other dairy beverages. Beverages that are typically *not* considered soft drinks include hot chocolate, hot tea, coffee, pure juice, milkshake, and etc. Soft drinks trace their history back to the mineral waters found in natural springs. Ancient societies believed that bathing in natural springs and/or drinking mineral waters could cure many diseases.

8.4.1 Carbonated drinks

In late 18th century, scientists made important progress in replicating naturally carbonated mineral waters. In 1767, Englishman Joseph Priestley first discovered a method of infusing water with carbon dioxide to make carbonated water when he suspended a bowl of distilled water above a beer vat at a local brewery in Leeds, England. His invention of carbonated water, (also known as soda water), is the major and defining component of most soft drinks. Priestley found water thus treated had a pleasant taste, and he offered it to friends as a refreshing drink. In 1772, Priestley published a paper entitled *Impregnating Water with Fixed Air* in which he describes dripping *oil of vitriol* (or sulfuric acid as it is now called) onto chalk to produce carbon dioxide gas, and encouraging the gas to dissolve into an agitated bowl of water.

Another Englishman, John Mervin Nooth, improved Priestley's design and sold his apparatus for commercial use in pharmacies. Swedish chemist Torbern Bergman invented a generating apparatus that made carbonated water from chalk by the use of sulfuric acid. Bergman's apparatus allowed imitation mineral water to be produced in large amounts. Swedish chemist Jöns Jacob Berzelius started to add flavors (spices, juices and wine) to carbonated water in the late 18th century.

8.4.2 Soft drink production

Soft drinks are made either by mixing dry ingredients and/or fresh ingredients (e.g. lemons, oranges, etc.) with water. Production of soft drinks can be done at factories, or at home. Soft drinks can be made at home by mixing either syrup or dry ingredients with carbonated water. Carbonated water is made using a home carbonation system or by dropping dry ice into water.

8.4.2.1 Ingredient quality

Of most importance is that the ingredient meets the agreed specification on all major parameters. This is not only the functional parameter, i.e. the level of the major constituent, but the level of impurities, the microbiological status and physical parameters such as color, particle size, etc. The size of bottles and price of soft drinks in different countries is different.

8.4.2.2 Producers

In every area of the world there are major carbonated beverage producers, however a few major North American companies are present in most of the countries of the world, such as Pepsi, and Coca Cola

8.4.2.3 Health effects

The consumption of sugar-sweetened soft drinks is associated with obesity, type 2 diabetes, dental cavities, and low nutrient levels. Experimental studies tend to support a causal role for sugar-sweetened soft drinks in these ailments, though this is challenged by other researchers. "Sugar-sweetened" includes drinks that use High-fructose corn syrup, as well as those using sucrose. Many soft drinks contain ingredients that are themselves sources of concern: caffeine is linked to anxiety and sleep disruption when consumed in excess, and the health effects of high-fructose corn syrup and artificial sweeteners remain controversial.

Sodium benzoate has been investigated as a possible cause of DNA damage and hyperactivity. Other substances have negative health effects, but are present in such small quantities that they are unlikely to pose any substantial health risk. Benzene belongs to this category: the amount of benzene in soft drinks is small enough that it is unlikely to pose a health risk.

For example, in 1998, the Center for Science in the Public Interest published a report titled *Liquid Candy: How Soft Drinks are Harming Americans' Health*. The report examined statistics relating to the soaring consumption of soft drinks, particularly by children, and the consequent health ramifications, including tooth decay, nutritional depletion, obesity, type-2 (formerly known as "adult-onset") diabetes, and heart disease. It also reviewed soft drink marketing and made various recommendations aimed at reducing soft drink consumption.



Chapter summary



- Fermentation usually implies that the action of microorganisms is desirable, and the process is used to produce alcoholic beverages such as beer, spirits and wine.
- Fermentation has various benefits. The primary benefit of fermentation is the conversion of sugars and other carbohydrates, e.g., converting juice into wine, grains into beer, carbohydrates into carbon dioxide to leaven bread, and sugars in vegetables into preservative organic acids.
- An alcoholic beverage is a drink containing ethanol.
- There are different the basic raw materials that can be used for manufacture of Beer, wine and distilled Spirit. Grains and fruits supplying carbohydrates are the basic raw materials
- Brewing is the production of alcoholic beverages and alcohol fuel through fermentation
- Similar to Beer, Wine has been made for several thousand years by fermentation of the juice of the grape.
- Various fermented products, upon distillation and aging, yield the distilled liquors. For example, Brandy is distilled from wine or from the marc, which is the pulp left by racking or straining
- A soft drink is a non-alcoholic beverage typically containing water; often carbonated water; and a flavoring agent.
- Soft drinks are made either by mixing dry ingredients and/or fresh ingredients (e.g. lemons, oranges, etc.) with water.
- Production of soft drinks can be done at factories, or at home. Soft drinks can be made at home by mixing either syrup or dry ingredients with carbonated water.



Self test exercises



1. Explain the major uses of fermentation
2. List the main raw materials used for manufacture of some of Alcoholic Beverages such as Beer, Spirit and wines
3. Compare and contrast the alcoholic content of fermented beverages and distilled spirit
4. What is soft drink? Mention the main raw materials for soft drink industry
5. Explain the difference between alcoholic drink and soft drink industry



Unit Introduction

Dear student, this chapter deals with Pharmaceutical Industry. We will also discuss Discovery and development of drugs, Classification and the chemistry of pharmaceutical products, Manufacturing of pharmaceutical products and Quality Control of Pharmaceuticals



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define Pharmaceutical Industry
- Discuss the discovery and development of drugs
- Explain Classification and the chemistry of pharmaceutical products
- Explain Manufacturing of pharmaceutical products
- Discuss Quality Control of Pharmaceuticals

9.1 Introduction

Dear student, Pharmaceutical industry is one of the most important sectors of health care worldwide. It produces many types of products. What is the basic difference among Pharmaceutical and other industries? Let warm up your self with the following activities.



Learning task 9.1



- a) Define Pharmaceutical Industry
- b) Explain major products of Pharmaceutical Industry
- c) Discuss the advantage of Pharmaceutical Industry to our day to activity

The pharmaceutical industry is one of the most important sectors of health care worldwide. Pharmaceutical products are all manufactured in very small quantities, but their production cost is exceedingly high; nearly 300 billion USD worldwide in 2005 (for various marketed drugs); this is expected to grow about 6-12% per year.

Pharmaceutical industries produce many types of products such as:

- Drugs used to treat various ailments (bacterial, viral, protozoal etc.)
- Agent used to supplement imbalances (electrolyte, metal salts, vitamins, hormones)
- Agents used for protection (contraceptives, vaccines etc.)
- Other health care products (antiseptic & disinfectants, ointments etc.)

9.2 Discovery and development of drugs

9.2.1 Introduction

Dear student, you have learnt that pharmaceutical industry is one of the most important sectors of health care worldwide which produces many types of products. Under this sub topic you learn the Discovery and development of drugs. Can you mention how drugs are discovered and developed? Lets warm up your self with the following activities.



Learning task 9.2



- Explain the Discovery and development of drugs
- List the two approaches which are used for discovery of new drug
- Discuss the process of Classical drug discovery and early development

Dear student, the development of a new drug is a long, tedious and expensive process. Most of the time it will take about 8-12 years (from new drug substance discovery to patentship). This process involves such steps as:-

- Discovery and early development phase
- Pre-clinical phase
- Clinical phase
- New drug administration (NDA) and post-marketing surveillance

Drug discovery process is always connected to the health problem that needs a cure. Two approaches are used for discovery of new drug. These are:

- Classical approach
- Modern approach

9.2.2 Classical drug discovery and early development

In classical drug discovery new drugs can be obtained from isolation/recovery from natural sources and their fermentation products and Chemical compounds, which were synthesized for this purpose. These compounds are tested on *in vitro* models (such as cell culture e.g. bacteria) and compounds that show positive effect are selected as hits and others are shelved. Then further research proceeds on *in vivo* model (i.e. on laboratory animals e.g. mouse) on which the diseases are artificially induced to confirm previous result and to investigate possible deleterious effects. A chemical substance that shows activity is called a **Lead** compound (a confirmed hit). Lead compounds are sometimes discovered incidentally and more often they are the results of long-term observation of nature. Chemical structure of the lead is elucidated and carefully analyzed to determine part of the molecule responsible for the pharmacological effect called **pharmacophore**. Other compounds (called **analogs**) are synthesized (keeping the pharmacophore groups the same) and tested again and again to change its physical and physiological properties compared to the lead and mostly until an optimal drug substance is obtained. This gives a **Structure–Activity Relationship (SAR)** data.

9.2.3 Modern drug discovery

Modern drug discovery is mostly started from natural ligand or modulator (receptor, enzyme etc). Here large number of synthetic or natural compounds (chemical library) is screened using semi/fully automated techniques such as NMR, plate readers and computers. The size of the library is increased continuously using high throughput synthesis such as *combinatorial synthesis*. This leads to the use of computerized robotic systems a very large number of reactions and assays. Discovery of a lead compound and its optimization then follows.

Table 9.1 Task and Drug discovery and early development

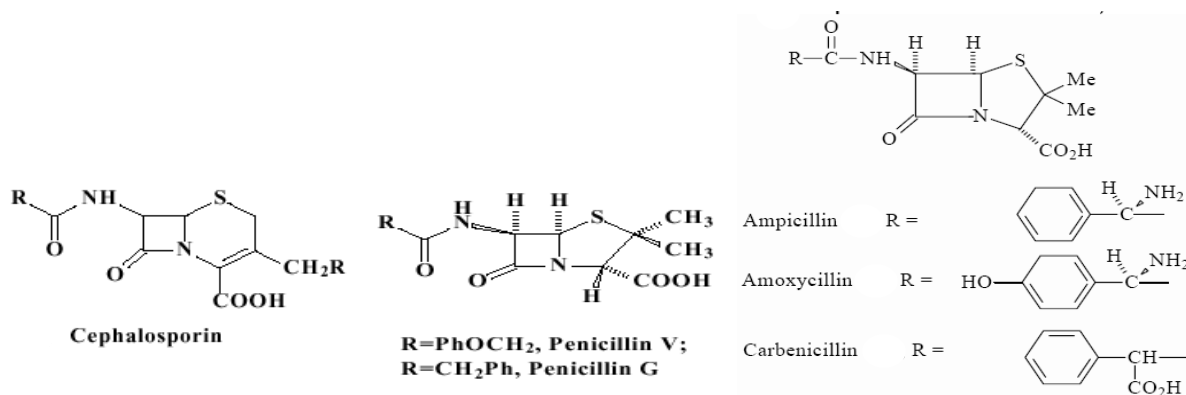
Discovery & early develop.	Classical approach	High throughput approach
Target identification	Based on medical symptoms	Based on receptor binding
Screening	Using laboratory animals or cell cultures	Using receptor binding assays with fast detection techniques
High confirmation lead	Use of second animal species	Use of second assay type
Lead optimization	Classical synthesis of 10-20 similar compounds, testing on laboratory animals	High throughput synthesis of 1000 to 100000 compounds tested with HTS receptor binding assays

Discovery and development of drugs

Example 1: Discovery penicillin

Dear student, do you know who discover Penicillin? Penicillin G was incidentally discovered by Alexander Fleming (in 1928) from a *contaminated* bacterial culture (by blue green mold; *P. notatum*). Then many modifications were made on this drug to change its therapeutic effect and spectrum of activity by:-

- i) Modification of the amino side chain gave various analogs
- ii) The replacement of the 5-membered thiazolidine ring to an analogous 6-membered ring leads to cephalosporin,
- iii) Further simplification of the structure to give clavulanic acid,



Example 2: Discovery of Acetyl salicylic acid (Aspirin™)

Dear student, the bark/leaves of willow tree was used since ancient time relief pain and fever. In 1832 the German chemist Piria isolated salicylic acid (SA) as the active substance in the plant material. SA became the lead substance for further development. SA was used as a pain remedy, but it has severe side effects when applied orally. In 1897 Felix Hoffmann, a chemist at Bayer AG, realized that the ester form of the ASA (acetylsalicylic acid) had less side effects and was even more efficacious than the free acid. Bayer marketed the ester under the trade name Aspirin.

About 80 years after the introduction ASA it was discovered to prevent heart attack and strokes and reduces the risk of sudden death due to heart attack. In 1982 John R. Vane was awarded the Nobel Prize for medicine for discovering the basic mechanism of action of acetylsalicylic acid.

9.3 Research and Development (R&D) of new drugs

Dear student, you have learnt the Discovery and Development of drugs, now you learn how Research and Development support for the Discovery of new drugs. Few kilogram of the test substance must be synthesized to have enough material for further testing. The research and development of new drugs include the following phases:

- Pre-clinical testing
- Clinical testing
- New drug administration (NDA)
- Post-marketing surveillance

i) Pre-clinical Testing

The objective of this phase is to assure that new substances are safe for humans before they are tested on patients. Some of the tasks conducted during this phase include:-

- Development of industrial synthesis method
- Determination of purity of drug substances
- Establishment of basic physical & chemical properties (e.g. water solubility and stability)
- Acute and chronic toxicity testing starts parallel to analytical studies
- Development of drug formulations containing the active ingredients

Analytical studies are carried by spectroscopic and chromatographic techniques. Single application of different doses of the test substance to rats or mice gives an indication of the acute oral toxicity.

The ADME (**A**bsorption, **D**istribution, **M**etabolism, and **E**limination) studies

i) Absorption:- to confirm the rate of drug substance entry into the blood stream

- It also measures the bioavailability

ii) Distribution:- to measure amount of substance that reaches to target organ and its accumulate in various organs.

iii) Metabolism:-measures chemical conversion of the substance in the body to other cpds

iv) Elimination:- describes the rate and route of elimination of metabolites from the body.

The ADME of the substance in the body is often studied with substances that have radioactive label in the molecule.

Table 9.2 Tasks in preclinical development

Preclinical phase	Typical tasks
Route of synthesis	Development of an industrial synthesis method
Properties and stability	Identification of impurities, Physicochemical properties, stability upon storage
Toxicity	Acute toxicity in rat & mice (single dose application) 4 week up to 2 years repeated dose toxicity in rat & dog Genetic toxicity in-vitro and in-vivo, e.g. mutagenicity Reproductivity toxicity in rat & rabbit
Pharmacokinetics and Metabolism (ADME)	Absorption in to blood circulation; Distribution in body; Metabolism (Chemical reactions) of drug in the body; Elimination of drug from the body
Development of Drug formulation	Development of tablets, syrups, injectables etc containing the drug substance

ii). Clinical Testing

After 3 to 5 years of research and development, the new drug substance can be applied to humans. Since clinical studies are conducted on humans, they are directed by physicians. Nevertheless clinical and analytical chemistry plays an important role in monitoring of the results of the test. This test is typically conducted in three phases, with each phase involving progressively more people.

Phase I

The substance is applied to healthy human volunteers, starting with a very low dose and then slowly increasing until the planned pharmaceutical dose is reached. The purpose of the test is two fold:

- ✓ The clinical parameters are monitored to detect any side effect, which may not have been observed in the animal tests.
- ✓ The second is to establish the pharmacokinetics in humans.
- ✓ Here blood samples are taken at predetermined intervals and analyzed for drug substance concentration usually by LC-MS-MS.

When a drug is administered orally as a tablet, it takes some time before it dissolves in the stomach and transferred to the blood circulation. During this absorption phase the level of the drug increases with time and reaches a maximum after about 1 to 2 hours. Soon after the drug reaches the circulation, it is also metabolized, mainly in the liver. The drug is slowly eliminated from the body and as a consequence the blood level and also the effect of the drug decrease.

Phase II

Potential drugs are first tested on selected patients for therapeutic efficacy in those disease states for which they are intended. NB- adverse effects be acceptably small

Phase III

- Involving a *larger group of patients*
- *Aimed at comparing* therapeutic outcome the new drug with standard treatments
- Strongly demands approval by institutional ethics committees according to international codes of conduct (Declarations of Helsinki, Tokyo, and Venice).

NB : -During clinical testing many drugs are revealed to be unusable.

-Ultimately only one drug from approximately 10,000 newly synthesized substances remains.

Table 9.3 Tasks in Clinical development and post marketing research

Clinical tests	Description of work
Phase 1	Testing of pharmacokinetics and side effects in healthy human volunteers
Phase 2	Proof of concept and efficiency in small group of human patients
Phase 3	Testing for efficacy and long term effects on many patients in different countries

iii) New drug approval (NDA)

Applicants submit appropriate test data (from preclinical and clinical trials).Then checked whether or not criteria of efficacy and safety have been met and product forms (tablet, capsule, etc.) satisfy general standards of quality control.

The new drug will then be marketed under a trade name and thus become available for prescription by physicians and dispensing by pharmacists. Decision to approve a new drug (NDA) is made by a national regulatory body



- Food & Drug Administration (FDA) in the U.S.A.
- Health Protection Branch Drugs Directorate in Canada, UK, Europe, Australia etc

iv) Post-marketing surveillance

Is to assessed benefit ratio and therapeutic value new drug after the drug gains more widespread use.

9.4 Classification and the Chemistry of Pharmaceutical products

Dear student, you have learnt that the Discovery and development of drugs is one of the most important sectors of health care worldwide which produces many types of products. Under this sub topic you learn the major Classification and the Chemistry of Pharmaceutical products. Can you mention how Pharmaceutical products can be classified? Let warm up your self with the following activities.

	Learning task 9.4	
<p>a) Explain the major classification of Pharmaceutical products</p> <p>b) Give examples of drugs that can be used as antibacterials, antibiotics antimalaria, antifungal and antiretroviral</p> <p>c) Compare and contrast Antiretroviral and Antibacterial drugs</p>		

Dear student, Pharmaceutical products can be classified based on:

- Pharmacologic effects they will produce
- Chemistry or
- Therapeutic target

Some of the common class of pharmaceuticals includes:

- | | |
|--------------------------------|-------------------------|
| ➤ Analgesics | ➤ Antiprotozoals |
| ➤ Antimicrobial and antibiotic | ➤ Antifungals |
| ➤ Antivirals | ➤ Antihelminthics etc.. |

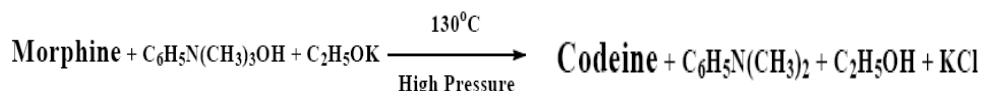
9.4. 1 The Analgesics

Dear student, Analgesics represent an important class of drugs that is used primarily to relief mild to severe pain. They are classified as *narcotic and non-narcotic*.

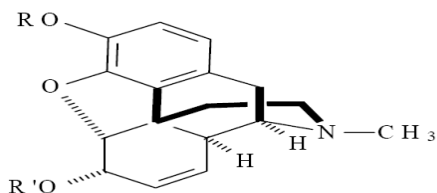
i) Narcotic analgesics (opiates)

- are natural or semisynthetic alkaloids obtained from Opium poppy
- Perhaps one of the oldest drugs known to man
- Include:

Morphine -for treating dull, constant pain and periodic pain.Codeine (methyl ether of morphine)- used for treating moderate pain and coughs.It is only 0.1 percent as active as morphine (lack free phenolic group)



Heroin;- more active than morphine by a factor of two.



R = R' = H Morphine

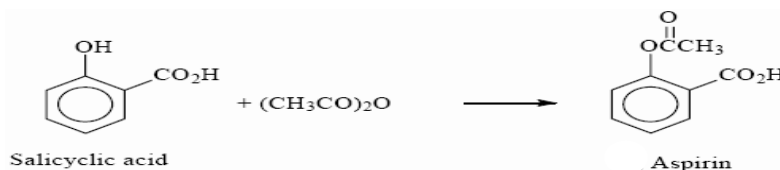
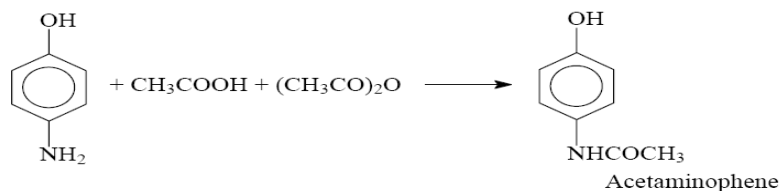
R = CH₃, R' = H Codeine

R = R' = CH₃ $\begin{matrix} \text{O} \\ \parallel \\ \text{C} \end{matrix}$ Heroin

II) Non-Narcotic analgesics (Non-opiates)

- Are widely used as nonprescription drugs.
- They are also efficient for the relief of mild pain and symptoms of rheumatoid arthritis.

Examples :-Acetaminophen; Aspirin , (S)-Naproxen, S-ibuprofen

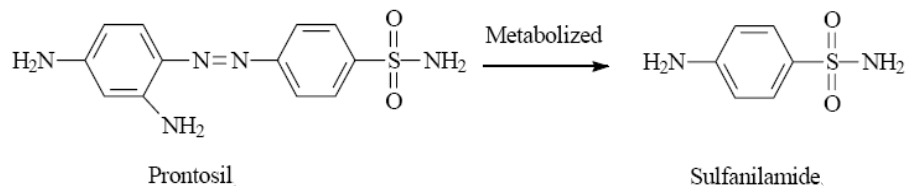


9.4.2 Antibacterials and Antibiotics

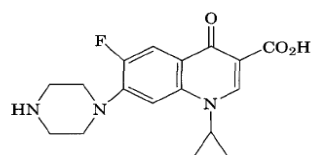
9.4.2.1 Synthetic antibacterials

a) Sulfonamides or sulfa drugs

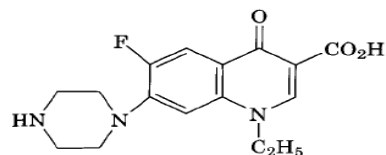
- Represent one of the oldest antibacterial agents discovered before penicillin. Currently used in combination with other antibacterials.



b) Quinolones



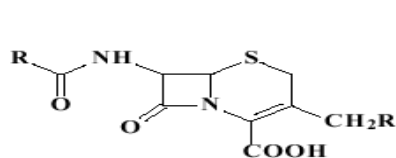
Ciprofloxacin



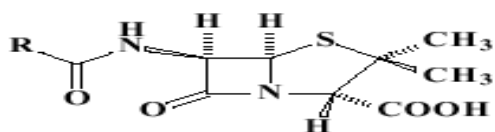
Norfloxacin

9.4.2.2 Natural & semi synthetic agents

a) β -Lactam antibiotics (*Penicillins and cephalosporins*)

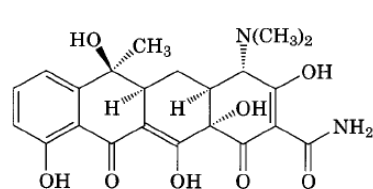


Cephalosporin

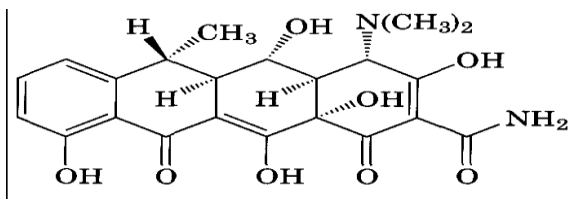


R=PhOCH₂, Penicillin V;
R=CH₂Ph, Penicillin G

b) Tetracyclines

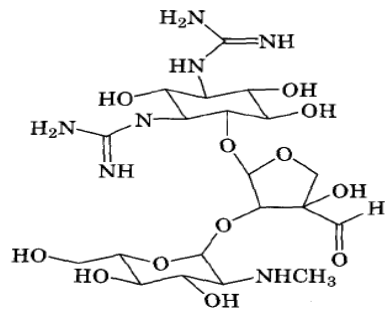


Tetracyclines

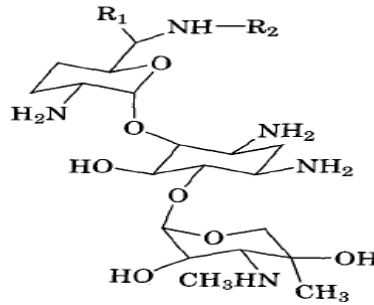


Doxycyclines

c) Aminoglycosides

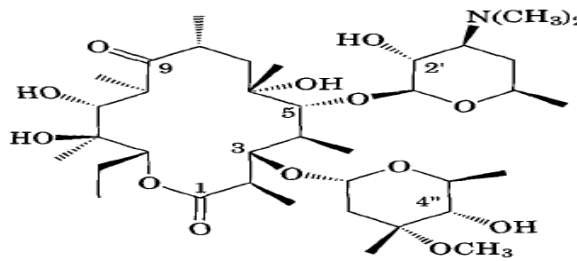


Streptomycin



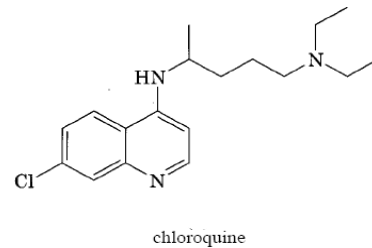
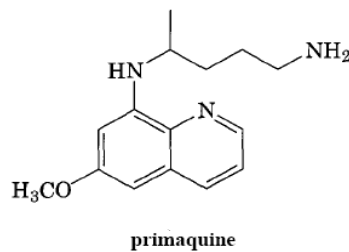
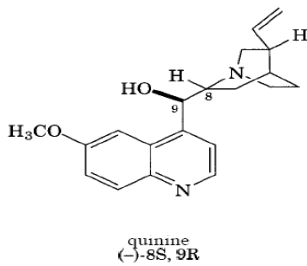
Gentamicin

d) Macrolides

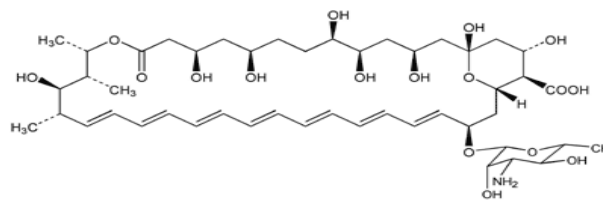


Erythromycin

9.4.3 Anti-malarial:- used for treatment of malaria; the common examples are quinine, primaquine and chloroquine



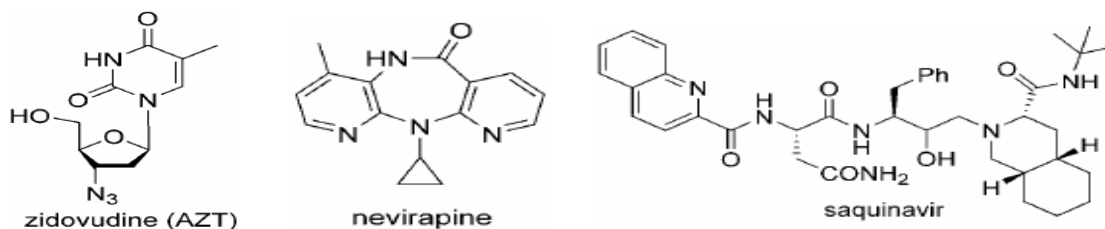
9.4.4 Anti-fungals used for treatment of fungi. E.g Polyenes (such as amphotericin B)



9.4.5 Antiretroviral drugs

Are drugs that can be used for Treatment of HIV AIDS; common examples are Nucleoside reverse transcriptase inhibitors (NRTIs) such as Zidovudine(AZT), Non-nucleoside reverse transcriptase inhibitors (NNRTIs) such as Nevirapine and Protease inhibitors (PIs) such as Saquinavir

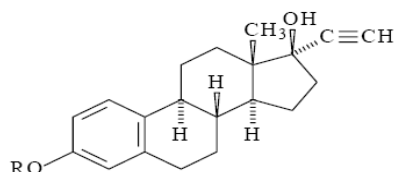
- i) Nucleoside reverse transcriptase inhibitors (NRTIs) e.g Zidovudine (AZT)
- ii) Non-nucleoside reverse transcriptase inhibitors (NNRTIs) e.g Nevirapine
- iii) Protease inhibitors (PIs) e.g Saquinavir



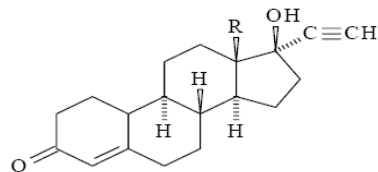
9.4.6 Oral contraceptives

The most common type of oral contraceptive is a combination of

- Synthetic estrogens:- e.g mestranol, ethinylestradiol and
- Synthetic progestin:- e.g levonorgestrel, norethynodrel



R = CH₃; Mestranol,
R = H; Ethinyl estradiol,



R = CH₂CH₃; Levonorgestrel,
R = CH₃; Norethynodrel,

9.5 Manufacturing of pharmaceutical products

Dear student, you have learnt that the major Classification and the Chemistry of Pharmaceutical products. Under this sub topic you learn Manufacturing of pharmaceutical products i.e., Pharmaceutical formulation /dosage forms. Can you mention some Pharmaceutical formulation /dosage forms that you know? Let warm up your self with the following activities.



Learning task 9.5



- a) Explain the most common dosage forms of pharmaceutical products
- b) Compare and contrast the Solid, Liquids and Semi-solid dosage forms

9.5.1 Pharmaceutical formulation /dosage forms

Dear student, Drug substances are seldom administered alone, but in combination with one or more non-medical agents that serve varied and specialized pharmaceutical functions such as solubilizing, suspending, thickening, diluting, emulsifying, stabilizing, preserving, coloring, flavoring etc. Pharmaceutical formulation is the process in which different chemical substances, including the active drug, are combined to produce a final medicinal product

A dosage form (DF) is the physical form of a dose of a chemical compound used as a drug intended for administration. The most common dosage forms of pharmaceutical products include

- ✓ Solid dosage forms: -Tablets, Capsules & powders
- ✓ Liquids dosage forms: - Solution, emulsion, suspension
- ✓ Semi-solid dosage forms: - Creams, Ointments
- ✓ Miscellaneous:- Aerosols, Patches

Tablets: - Are the most popular type of pharmaceutical dosage form that offers convenience, stability, accuracy and precision, and bioavailability active ingredients. They are usually compressed preparation that contains

- 5-10% of the drug (active substance) and
- 80% of fillers, disintegrants, lubricants, glidants, and binders (collectively called excipients)

Each of these components has the following function

- i) Fillers (e.g sugar, starch):- added to dilute the active ingredient to the correct concentration.
- ii) Binders (e.g corn syrup, starch):- is needed to bind tablet particles together
- iii) Lubricants (e.g magnesium stearate, polyethylene glycol):- added to facilitate equipment operation, or to slow disintegration or dissolution of the active ingredient.

Capsules:- Gelatinous envelope enclosing the active substance. They are the most common solid oral dosage form consumed after tablets. Capsules can be designed to remain intact for some hours after ingestion in order to delay absorption. It may also contain a mixture of slow- and fast-release particles to produce rapid and sustained absorption in the same dose

Liquid Dosage Forms: - are prepared by dissolving the ingredients in the appropriate solvent systems. Dyes, flavors, sweeteners, and antimicrobial preservatives are added to mask unpleasant taste or appearance, and to prevent mold and bacterial growth. If the liquid is to be used for injection or ophthalmic use, sterilization is required. But solutions for external or oral use do not require sterilization but generally contain antimicrobial preservatives. Common liquid dosage forms include:



- Creams – Are emulsion of oil and water in approximately equal proportions. Penetrates stratum corneum outer layer of skin well.
- Ointments- Are effective barriers against moisture loss composed of oil (80%) and water (20%).

- Pastes – are ointment in to which powder is suspended.
- Gels - Liquefies upon contact with the skin.

Suppositories: - Suppositories are semi-rigid and plastic dosage forms designed to be delivered to body cavities, such as the rectum, vagina, or urethra. They either melt at body temperature (if made with cocoa butter) or dissolved in the fluid of the cavity (if made with polyethylene glycols or glycerol gelatin). Suppositories can be used for systemic therapy (rectal suppositories) or local treatment. Cocoa-butter-based suppositories can be prepared manually by pharmacists by mixing the ingredients to a pliable consistency in a mortar.

9.6 Quality Control of Pharmaceuticals

Dear student, you have learnt that the Manufacturing of pharmaceutical products. Under this sub topic you learn Quality Control of Pharmaceuticals. Can you explain how Quality Control of Pharmaceuticals can be implemented? Let warm up your self with the following activities.

	Learning task 9.6	
<p>a) List some criteria that can be used to monitor the level of quality Pharmaceuticals</p> <p>b) Compare and contrast Quality Control of tablets and capsules and injectable solutions</p>		

Dear student, various chemical, physical and biological tests are provided to ensure the required high standards of safety, purity, and effectiveness of drugs. The drug agencies monitor the levels of quality control through its good- manufacturing practices (GMP) and factory inspections.

Things that are controlled during GMP inspection include:

- | | |
|--|---|
| <ul style="list-style-type: none"> ➤ Appropriateness of qualified and trained personnel; ➤ Adequacy of premises and space ➤ Suitability of equipment and services | <ul style="list-style-type: none"> ➤ Correctness of materials, containers and labels ➤ Approval of procedures and instructions ➤ Suitability of storage and transportation systems |
|--|---|

9.6.1 Quality Control of tablets and capsules

Tablets and capsules are examined for the following properties:

- Identity
- Content of active drug
- Size
- Physical appearance
- Disintegration and/or dissolution time
- Friability (mechanical stability of tablets)
- Variability in weight

9.6.2 Quality Control of injectable solutions

All are tested for sterility and the absence of pyrogens. Various spectroscopic techniques, such as HPLC, and other analytical techniques are used in the quality control laboratory to determine the purity and the amount of the active drug present in the different dosage forms.



Chapter summary



- The pharmaceutical industry is one of the most important sectors of health care worldwide
- Drug discovery process is always connected to the health problem that needs a cure. Two approaches are used for discovery of new drug are the Classical approach and Modern approach
- In classical drug discovery new drugs can be isolated /recovered from natural sources and their fermentation products or synthesized for this purpose.
- Modern drug discovery natural ligand or modulator molecules (to a receptor, enzyme etc) or synthetic/natural compounds (in chemical library) are screened to discover a lead compound.
- Optimization of the lead compound then follows in four phases: Pre-clinical testing; Clinical testing; New drug administration (NDA) and Post-marketing surveillance
- Pharmaceutical products can be classified based on Pharmacologic effects they will produce, their Chemistry or Therapeutic target. Some of the common class of pharmaceuticals includes: Analgesics, Antimicrobials and antibiotics, Antivirals, Antiprotozoals , Antifungals, Anthelmintics etc.
- Drug substances are seldom administered alone, but in combination with one or more non-medical agents that serve varied and specialized pharmaceutical functions such as solubilizing, suspending, thickening, diluting, emulsifying, stabilizing, preserving, coloring, flavoring etc.
- Various chemical, physical and biological methods are used to tests safety, purity, and effectiveness of drugs.



Self test exercises



- Compare and contrast Classical and Modern approaches to drug discovery
- The development of a new drug is a long, tedious and expensive process. Explain?
- Explain how Pharmaceutical products can be classified and state some common class of pharmaceuticals agents available in the market.
- Drugs are mostly prepared by mixing therapeutically active agents with one or more non-medical agent. Explain why is this so? Discuss how the inspection
- Discuss how the inspection and quality control of pharmaceuticals carried



Unit Introduction

Dear student, this chapter deals with Chemicals for Agriculture. We will discuss some of the chemicals such as Insecticides, DDT, BHC and Parathion, Fungicides and 2,4,6-Trichloro Phenol, Herbicides–2,4-D and 2,4,5-T, that are used in Agricultural activities.



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Mention some of common chemicals that can be used for Agricultural activity.
- Define Insecticides
- Explain the use of insecticides
- Explain the use of DDT, BHC , Parathion, Fungicides , 2,4,6-Trichloro Phenol in Agricultural activities
- Define Herbicides
- Compare and contrast insecticide and herbicides
- Explain the basic difference between organochloro pesticides and organophosphate pesticides
- Explain how pesticides cause environmental pollution

10.1 Introduction to Insecticides

Dear student, there are many common chemicals that can be used in Agricultural activity. The main use of these chemicals is to kill pests, herbs so that agricultural crops and cereals can be protected from pests. Can you tell to your friend what Insecticides are? Let warm up your self with the following activities.



Learning task 10.1



- a) Define insecticides
- b) Mention some of common chemicals that can be used as insecticide
- c) Explain the use of insecticides in Agricultural activity

Insecticides are agents of chemical or biological origin that control insects. Control may result from killing the insect or otherwise preventing it from engaging in behaviors deemed destructive. Insecticides may be natural or manmade and are applied to target pests in a myriad of formulations and delivery systems (sprays, baits, slow-release diffusion, etc.).

The science of biotechnology has, in recent years, even incorporated bacterial genes coding for insecticidal proteins into various crop plants that deal death to unsuspecting pests that feed on them. Some 10,000 species of the more than 1 million species of insects are crop-eating, and of these, approximately 700 species worldwide cause most of the insect damage to man's crops, in the field and in storage. Humanoids have been on earth for more than 3 million years, while insects have existed for at least 250 million years.

We can guess that among the first approaches used by our primitive ancestors to reduce insect annoyance was hugging smoky fires or spreading mud and dust over their skin to repel biting and tickling insects, a practice resembling the habits of elephants, swine, and water buffalo. Today, such approaches would be classed as *repellents*, a category of *insecticides*.

10.2 DDT and Organochlorine Insecticides

Dear student, you have learnt that Insecticides are agents of chemical or biological origin that control insects. Under this sub topic you learn DDT and Organochlorine Insecticides. Can you mention some of Organochlorine Insecticides? Let warm up your self with the following activities.



Learning task 10.2



- a) Define Organochlorine insecticides
- b) Compare and contrast DDT and BHC
- c) Explain why DDT is banned from the market

Chlorinated hydrocarbon or organochlorine insecticides are hydrocarbon compounds in which various numbers of hydrogen atoms have been replaced by Cl atoms. The structural formulas of some chlorinated hydrocarbon insecticides are shown below. It can be seen that the structural formulas of many of these insecticides are very similar; dieldrin and endrin are stereoisomers. The most commonly used insecticides in the 1960s; these compounds have been largely phased out of general use because of their toxicities, and particularly their accumulation and persistence in food chains. They are discussed briefly here, largely because of their historical interest, and because their residues in soils and sediments still contribute to water pollution.

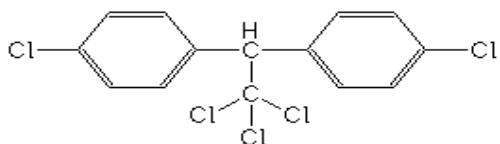
10.2.1. DDT

DDT the first of the chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceutical in Switzerland discovered the effectiveness of DDT as an insecticide he was awarded the Nobel Prize in medicine and physiology in 1948 for this discovery. Of the organochlorine insecticides, the most notable has been DDT (dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), which was used in massive quantities following World War II. It has a low acute toxicity to mammals, although there is some evidence that it might be carcinogenic.

DDT is a very persistent insecticide and accumulates in food chains. It has been banned in the U.S. since 1972. For some time, **methoxychlor** was a popular DDT substitute, reasonably

biodegradable, and with a low toxicity to mammals. Structurally similar **chlordane**, **aldrin**, **dieldrin/endrin**, and **heptachlor**, all now banned for application in the U.S., share common characteristics of high persistence and suspicions of potential carcinogenicity.

Reports indicated that harmless insects (such as bees), fish, birds, and other animals were being killed or harmed as a result of exposure to DDT. DDT's environmental problems arise because of two important properties: **persistence and lipid-solubility**. The term persistence refers to the fact that DDT does not break down very easily. Once the pesticide has been used in an area, it is likely to remain there for many years. In addition, DDT does not dissolve in water, although it does dissolve in fatty or oily liquids.

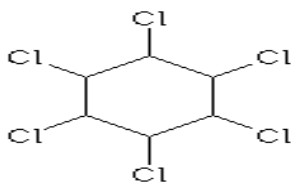


Structure of DichloroDiphenylTrichloroethane(DDT)

10.2.2 BHC (1, 2,3,4,5,6-Hexachlorocyclohexane)

Hexchlorocyclohexane (HCH)--Also known as **benzenehexachloride (BHC)**, the insecticidal properties of HCH were discovered in 1940 by French and British entomologists. In its technical grade, there are five isomers, *alpha*, *beta*, *gamma*, *delta* and *epsilon*. Surprisingly, only the *gamma* isomer has insecticidal properties. Consequently, the *gamma* isomer was isolated in manufacture and sold as the odorless insecticide *lindane*. Only the gamma isomer is effective as an insecticide, whereas the other isomers give the product a musty odor and tend to undergo bioaccumulation.

In contrast, technical grade HCH has a strong musty odor and flavor, which can be imparted to treated crops and animal products. Because of its very low cost, HCH is still used in many developing countries A formulation of the essentially pure gamma isomer has been marketed as the insecticide called **lindane**.



Structure of BHC (1,2,3,4,5,6-Hexachlorocyclohexane)

Mode of action:-The effects of HCH superficially resemble those of DDT, but occur much more rapidly, and result in a much higher rate of respiration in insects. The *gamma* isomer is a neurotoxicant whose effects are normally seen within hours as increased activity, tremors, and convulsions leading to prostration. It too, exhibits a negative temperature correlation, but not as pronounced as that of DDT.

10.3 Organophosphate Insecticides

Dear student, you have learnt that DDT and Organochlorine Insecticides. Under this sub topic you learn Organophosphate Insecticides. Can you mention some of Organophosphate Insecticides? Let warm up your self with the following activities.



Learning task 10.3



- a) Define Organophosphate Insecticides
- b) Mention some of Organophosphate Insecticides
- c) Compare and contrast Organochlorine Insecticides and Organophosphate insecticides
- d) Compare and contrast parathion and malathion

Organophosphate insecticides are insecticidal organic compounds that contain phosphorus, some of which are organic esters of orthophosphoric acid, such as paraoxon:

10.3.1 Parathion

More commonly, insecticidal phosphorus compounds are **phosphorothionate compounds, such as parathion or chlorpyrifos**, the toxicities of organophosphate insecticides vary a great deal. For example, as little as 120 mg of parathion has been known to kill an adult human, and a dose of 2 mg has killed a child. Most accidental poisonings have occurred by absorption through the skin. Since its use began, several hundred people have been killed by parathion. In contrast, **malathion** shows how differences in structural formula can cause pronounced differences in the properties of organophosphate pesticides.

The biodegradation of these compounds is an important chemical process. Fortunately, unlike the organohalide insecticides that they largely displaced, the organophosphates readily undergo biodegradation and do not bioaccumulate.

10.3.2 Malathion

Malathion has two carboxyester linkages which are hydrolyzable by carboxylase enzymes to relatively nontoxic products as shown by the following reaction: The enzymes that accomplish malathion hydrolysis are possessed by mammals, but not by insects, so mammals can detoxify malathion and insects cannot. The result is that malathion has selective insecticidal activity.

For example, although malathion is a very effective insecticide, its LD₅₀ (dose required to kill 50% of test subjects) for adult male rats is about 100 times that of parathion, reflecting the much lower mammalian toxicity of malathion compared to some of the more toxic organophosphate insecticides, such as parathion. Unlike the organohalide compounds they largely displaced, the organophosphates readily undergo biodegradation and do not bioaccumulate. Because of their high biodegradability and restricted use, organophosphates are of comparatively little significance as water pollutants.

10.4 Carbamates

Dear student, you have learnt that Organochlorine Insecticides and Organophosphate Insecticides. Under this sub topic you learn about carbamates. What are carbamates? Let warm up your self with the following activities.



Learning task 10.4



- a) Define carbamates.
- b) Explain why Carbamate pesticides have been widely used among the rest pesticides

Pesticidal organic derivatives of carbamic acid, are known collectively as **carbamates**. Carbamate pesticides have been widely used because some are more biodegradable than the formerly popular organochlorine insecticides, and have lower dermal toxicities than most common organophosphate pesticides. **Carbaryl** has been widely used as an insecticide on lawns or gardens. It has a low toxicity to mammals. **Carbofuran** has high water solubility and acts as a plant systemic insecticide. As a plant systemic insecticide, it is taken up by the roots and leaves of plants so that insects are poisoned by the plant material on which they feed.

10.5 Fungicides and 2, 4, 6-Trichlorophenol

10.5.1 Fungicides

Dear student, you have learnt the use of Organochlorine Insecticides, Organophosphate Insecticides and carbamates in agricultural activities. Under this sub topic you learn about Fungicides and 2,4,6-Trichlorophenol. What are Fungicides and 2, 4, 6-Trichlorophenol? Let warm up your self with the following activities.



Learning task 10.5



- Define Fungicides
- Discuss the major uses of Fungicides and 2, 4, 6-Trichlorophenol
- Mention the health and environmental effects of 2, 4, 6-Trichlorophenol

Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality and profit. Fungicides are used both in agriculture and to fight fungal infections in animals. Chemicals used to control oomycetes, which are not fungi, are also referred to as fungicides as oomycetes use the same mechanisms as fungi to infect plants. Fungicides can either be *contact*, *translaminar* or *systemic*.

- Contact fungicides** are not taken up into the plant tissue, & only protect the plant where the spray is deposited;
- Translaminar fungicides** redistribute the fungicide from the upper, sprayed leaf surface to the lower, unsprayed surface;
- Systemic fungicides** are taken up & redistributed through the xylem vessels to the upper parts of the plant.

The most common active ingredient in fungicides is sulfur, present at 0.08% in weaker concentrates, and as high as 0.5% for more potent fungicides. Fungicides in powdered form are usually around 90% sulfur and are very toxic. Other active ingredients in fungicides include neem oil, rosemary oil, jojoba oil, and the bacterium *Bacillus subtilis*. Fungicide residues have been found on food for human consumption, mostly from post-harvest treatments. Some fungicides are dangerous to human health, such as vinclozolin, which has now been removed from use.

10.5.2 2, 4, 6-Trichlorophenol

2, 4, 6-Trichlorophenol, also known as TCP, phenaclor, Dowicide 2S, Dowcide 2S, omal, is a chlorinated phenol that has been used as a fungicide, herbicide, insecticide, antiseptic, defoliant, and glue preservative. It is a yellow solid with a strong, sweet odour. It decomposes on heating to produce toxic and corrosive fumes including hydrogen chloride and chlorine.

10.5.2.1 Health effects

2, 4, 6-Trichlorophenol is carcinogenic in animals, causing lymphomas, leukemia, and liver cancer via oral exposure. It is classified as *Group B2* (probable human carcinogen) by the United States Environmental Protection Agency. 2,4,6-Trichlorophenol is reasonably anticipated to be a human carcinogen based on limited evidence for the carcinogenicity of combined exposures to polychlorophenols, including 2,4,6-trichlorophenol, in humans and sufficient evidence for the carcinogenicity of 2,4,6-trichlorophenol in experimental animals.

10.5.2.2 Environmental effects

2,4,6-Trichlorophenol is an environmental pollutant that has been found in fresh water lakes such as the Great Lakes.

10.5.2.3 Uses

2,4,6-Trichlorophenol has been used primarily in various pesticide formulations and as a wood preservative. These have included fungicides, glue preservatives, insecticides, bactericides, and as an antimildew agent for textiles.

10.6 Chlorophenoxy Herbicides: 2,4-D and 2,4,5-T

Dear student, you have learnt the use of Fungicides and 2,4,6-Trichlorophenol in agricultural activities. Under this sub topic you learn about Herbicides-2,4-D and 2,4,5-T. What are Herbicides? Let warm up your self with the following activities.



Learning task 10.6



- What are Chlorophenoxy Herbicides?
- Explain the use of 2,4-D and (2,4,5-T)
- Mention the health and environmental effects of 2,4-D and (2,4,5-T)

Dear student, The Chlorophenoxy Herbicides, including 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), were manufactured on a large scale for weed and brush control and as military defoliants.

10.6.1. 2, 4-D (2, 4-dichlorophenoxy acetic acid)

The herbicide 2, 4-D was first identified in 1942 and marketed in 1944. Despite its decades of usage, there are still data gaps concerning 2, 4-D's effects on human health and environment risk.

10.6.1.1 What is 2, 4-D?

One of the hormone weedkillers, 2,4-D (2,4-dichlorophenoxy acetic acid) is an aryloxyalkanoic acid known also as a 'phenoxy herbicide', which includes MCPA, (2-methyl-4-chlorophenoxyacetic acid) mecoprop, triclopyr and 2,4,5-T. These chemicals have complex mechanisms of action against weeds, resembling those of auxins (growth hormones). Once absorbed 2,4-D is translocated within the plant and accumulates at the growing points of roots and shoots where it inhibits growth.

The principal use is for the control of broad leaf weeds in cereal crops-including wheat, maize, rice and sorghum-and grassland and turf areas. It is also widely used in mixtures with other herbicides to provide weed control in forestry, orchards and non-crop areas, and for the control of aquatic weeds. The phenoxy acid group of herbicides are probably one of the widest used herbicide chemical classes. The US, South America, Europe and the former Soviet Union are major markets for 2,4-D-weed control on US wheat relies on little else-and global use is predicted to grow over the next decade.

10.6.1.2 Acute toxicity of 2,4-D

2, 4-D is a WHO Class II 'moderately hazardous' pesticide. This places it in the same class as endosulfan, lindane, paraquat and toxaphene. It has an LD₅₀ of 375 mg/kg in the rat with evidence suggesting a similar level of toxicity in humans. Occupational exposure to 2, 4-D has produced serious eye and skin irritation. Other symptoms of 2, 4-D poisoning include nausea, weakness and fatigue, and in some cases neurotoxic effects including inflammation of nerve endings. Some medical reports from practitioners who have treated victims of acute exposure to

2,4-D mention severe and sometimes long lasting or even permanent symptoms. These include, as well as those listed above, diarrhoea, temporary loss of vision, respiratory tract irritation, confusion, numbness and tingling, bleeding and chemical hypersensitivity.

10.6.1.3 Chronic effects of 2, 4-D

It seems that long term exposure to 2, 4-D can affect different animals in a wide variety of ways. Rats for example were found to be largely unaffected when fed moderately large amounts in their diet over long periods, although signs of kidney pathology were demonstrated. Dogs however died when fed smaller amounts over shorter periods. A human fed 16.3 grammes over 32 days showed severe symptoms of intoxication. It also seems that the various chemical forms of 2, 4-D can have different toxic effects. Acid, salt and various esters differ in all their measured toxic effects to some extent, but the majority of toxicity data relates only to the acid.

10.6.1.3 Fate in the environment

2, 4-D has low soil sorption and a high potential for leachability. Indeed 2, 4-D residues have been recorded many times both in Water Company monitoring programmes and by the UK Department of the Environment. It has also been detected in groundwater supplies in a number of US States and in Canada. In 1994, 3% of groundwater samples, and in 1995, 4% of surface water samples in England and Wales exceeded the EU standard. Some formulations of 2, 4-D are highly toxic to fish while others are less so. Aquatic invertebrates do not in general seem to be very sensitive to 2, 4-D. Moderate exposure of honey bees to 2, 4-D severely impaired reproduction.

10.6.2. 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)

Dear student, 2, 4, 5-Trichlorophenoxyacetic acid (2, 4, 5-T) was a widely used broadleaf herbicide until being phased out starting in the late 1970s. While 2, 4, 5-T itself is of only moderate toxicity, the manufacturing process for 2, 4, 5-T contaminates this chemical with trace amounts of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD). TCDD is extremely toxic to humans. With proper temperature control during production of 2, 4, 5-T, TCDD levels can be held to about .005 ppm. Before the TCDD risk was well understood, early production facilities lacked proper temperature controls. Individual batches tested later were found to have as much as 60 ppm of TCDD.

2,4,5-T was withdrawn from use in the USA in 1983, at a time of heightened public sensitivity about chemical hazards in the environment. Public concern about dioxins was high, and production and use of other (non-herbicide) chemicals potentially containing TCDD contamination was also withdrawn. These included pentachlorophenol (a wood preservative) and PCBs (mainly used as stabilizing agents in transformer oil). 2,4,5-T has since largely been replaced by dicamba and triclopyr.

2,4,5-T (2,4,5-trichlorophenoxyacetic acid) is the chemical which received notoriety after it was extensively used as a defoliant in the Vietnam war. It is closely related to a number of other herbicides, such as 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (2-methyl-4-chlorophenoxyacetic acid), which are plant growth stimulants which cannot be metabolised by plants. Therefore if they are applied in high concentrations they cause lethal, uncontrollable and grossly distorted growth. 2,4-D and MCPA were the first hormone herbicides and the first really selective weedkillers, which killed weeds but did not harm other plants or animals. 2,4-D is still extensively used in the USA, but in the UK MCPA is more commonly used, especially in the form of a combined fertiliser/weedkiller for controlling dandelions and daisies in lawns.

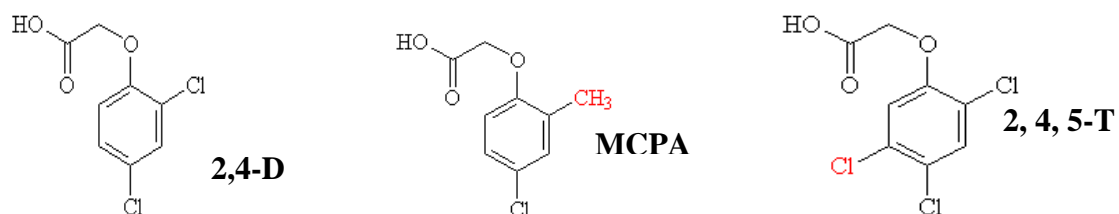


Fig 10.6.2 Structure of 2, 4-D; MCPA & 2,4,5-T

10.7 Pesticides pollution

Dear student, you have learnt that Chlorophenoxy Herbicides, including 2, 4-D and 2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T), were manufactured on a large scale for weed and brush control and as military defoliants. Under this sub topic you learn about Pesticides pollution. How pesticides can cause pollution? Let warm up your self with the following activities.



Learning task 10.7



- a) Discuss pesticide pollution
- b) Explain how pesticides pollute the soil and wild life
- c) Explain how human being can be exposed to pesticide pollution

Pesticides are a cause of pollution, affecting **land** and **water** in particular. The problem is huge and growing. **For example:** In the US pesticides pollution has been found in *nearly every lake, river and stream*, according to a US Geological Survey in the 1990s. Pesticides cause pollution by running off agricultural fields and from horticultural land and domestic gardens, too. Rain water washes the chemicals into nearby water sources. Here are some of the bad effects of pesticides.

10.7.1 Pesticides and pollution of the soil

Pesticides decrease biodiversity in the soil because they do not just kill the intended pest; they often kill many of the other small organisms present. When life in the soil is killed off, the soil quality deteriorates and this has a knock-on effect upon the retention of water. This is a problem for farmers particularly in times of drought. At such times, organic farms have been found to have yields 20-40% higher than conventional farms. Soil fertility is affected in other ways, too. When pesticides kill off most of the active soil organisms, the complex interactions which result in good fertility break down.

10.7.2 Harmful pesticides and wildlife

Dear student, Pesticides have other bad effects on the eco-system. The misuse of pesticides can cause valuable pollinators such as bees and hover-flies to be killed and this in turn can badly affect food crops. Many pesticides contain chemicals which are persistent soil contaminants. Their effects may last for years. For example, Amphibians such as frogs are particularly vulnerable to concentrations of pesticides in their habitat.

Atrazine, one of the world's most popular weed killers, has been found to feminize frogs, leading to sterility in males. It is still in use in the US, with about 80 million pounds being applied annually, but has been banned in the EU countries since 2004. It may also affect male fertility in humans and is a known endocrine disruptor. This is a fairly typical example of pesticides and pollution which results, affecting the lives of people and wildlife alike. Because of the profits to be made most companies are slow to accept responsibility and the problem is hidden by the use of numerous trade names for the one chemical.

10.7.3 Pesticides and human health

Pesticides can also endanger workers during production, transportation, or during and after use. Bystanders may also be affected at times, for example walkers using public rights of way on adjacent land or families whose homes are close by crop spraying activities. One of the main hazards of pesticide use is to farm workers and gardeners.

10.7.4 Diet as a source of exposure

Exposure to pesticides for most people is through diet. A study in 2006 measured organophosphorus levels in 23 school children before and after changing their diet to organic food. The levels of organophosphorus exposure dropped immediately and dramatically when the children began the organic diet. Residues, set by governments, are limited to tolerance levels that are considered safe, based on average daily consumption of these foods by adults and children.



Chapter summary



- Insecticides are agents of chemical or biological origin that control insects.
- Insecticides may be natural or manmade and are applied to target pests in a myriad of formulations and delivery systems (sprays, baits, slow-release diffusion, etc.).
- Chlorinated hydrocarbon or organochlorine insecticides are hydrocarbon compounds in which various numbers of hydrogen atoms have been replaced by Cl atoms.
- DDT the first of the chlorinated organic insecticides, which is a very persistent insecticide and accumulates in food chains
- Organophosphate insecticides are insecticidal organic compounds that contain phosphorus, some of which are organic esters of orthophosphoric acid, such as paraoxon
- Carbamate pesticides have been widely used because some are more biodegradable than the formerly popular organochlorine insecticides, and have lower dermal toxicities than most common organophosphate pesticides.
- Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores
- 2, 4, 6-Trichlorophenol, also known as TCP, is a chlorinated phenol that has been used as a fungicide, herbicide, insecticide, antiseptic, defoliant, and glue preservative.
- One of the hormone weedkillers, 2,4-D (2,4-dichlorophenoxy acetic acid) is an aryloxyalkanoic acid known also as a 'phenoxy herbicide', which includes MCPA, (2-methyl-4-chlorophenoxyacetic acid) mecoprop, triclopyr and 2,4,5-T.
- 2, 4, 5-Trichlorophenoxyacetic acid (2, 4, 5-T) was a widely used broadleaf herbicide until being phased out starting in the late 1970s.
- Pesticides are a cause of pollution, affecting land and water in particular.
- Generally Pesticides are a cause of pollution, affecting soil, wild life and human health



Self test exercises



1. Insecticides are agents of chemical or biological origin that control insects
 - a) Mention some of common chemicals that can be used as insecticide
 - b) Explain the use of insecticides in Agricultural activity
2. Compare and contrast Organochlorine Insecticides and Organophosphate insecticides
3. Compare and contrast parathion, Malathion and carbamates
4. Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores
 - a) Discuss the major uses of Fungicides
 - b) Mention the health and environmental effects of Fungicides
5. 2,4-D and (2,4,5-T) are some of common Chlorophenoxy Herbicides
 - a) Explain the use of 2,4-D and (2,4,5-T)
 - b) Mention the health and environmental effects of 2,4-D and (2,4,5-T)
6. Pesticides are a cause of pollution, affecting soil, wild life and human health
 - a) Explain how pesticides pollute the soil and wild life
 - b) Mention some of the exposure route how human being can be exposed to pesticide pollution



Unit Introduction

Dear student, this chapter deals with Dyestuff. We will also discuss about Dyes, Color and constitution, Methods of dyeing and Classification of dyes



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define dye
- Explain the relation ship between color and constitution
- Define Insecticides
- Explain methods of dyeing
- Explain how dyes are classified

11.1. Introduction to dyes

Dear student, Dyes are colored organic compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. Can you tell the history of dyes? Let warm up your self with the following activities.



Learning task 11.1



- a) Define Dyes
- b) Explain the history of dye industry

Indigo was the oldest known dye used by the ancient Egyptians to dye mummy clothes. The industry has lately experienced major setbacks in terms of profitability and overall attractiveness particularly in Europe and the United States. Major changes have taken place during the last 20

years. Nowadays Asia (India, Japan, Korea and China) has become the largest dyestuff market, accounting for about 42% of the value of the global dyestuff market.

11.2 Color and Constitution

Dear student, you have learnt what dyes are and their history. Under this sub topic you learn about Color and Constitution. Can you explain the relationship between Color and Constitution?

Let warm up your self with the following activities.



Learning task 11.2



- a) Mention the two major types of colorants produced today
- b) Define Color Index
- c) Discuss the effect of structure on color observed
- d) Explain how auxochromes and chromophores influence color intensity of a dye

11.2.1 Colorants

The two major types of **colorants** produced today are **dyes** and **pigments**.

Pigments (both inorganic and organic types) are almost always applied in an aggregated or crystalline insoluble form that requires a binder to form a coating on the surface of a substrate. They do not interact with the substrate and hence do not destroy the crystal structure of the substrate

Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance. The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied. The primary use of dyes is:

- In the textile industry, although substantial quantities are consumed for coloring,
- Such diverse materials as leather, paper, plastics, petroleum products, and food.

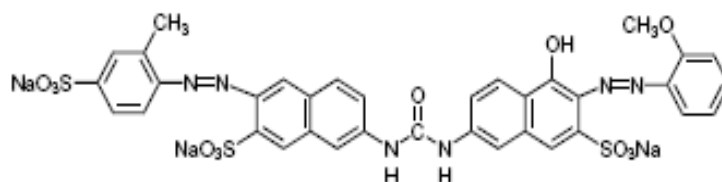
To be of commercial interest, dyes must have high color intensity and produce dyeing of some permanence. The color intensity of the dye molecule depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 700 nm. The partial structures necessary for color (unsaturated groups that can undergo $\pi-\pi^*$ and $n-\pi^*$ transitions) were called

chromophores :For example: C- C , -C= C- , -N= N- , -NO₂ , and etc. It was also observed that the presence of some other groups caused an intensification of color. These groups are called *auxochromes*. The auxochromes are groups that can not undergo π - π^* transitions, but can undergo transition of n electrons: -OH, -OR, -NH₂, -NHR, -NR₂, -X

11.2.2 Color Index

Dear student, The Color Index (CI) is a list of identification numbers and names given to individuals pigments and dyes used in, among other things, art materials. It also serves as a reference source for both the chemical structure and technical properties of dyes. It is published by the Society of Dyers and Colorists (UK) and Association of Textile Chemists and Colorists (USA). The Color Index has three parts:

- Use (which state whether it's a pigment or dye)
- Color (indicated by a pigment code and number)
- Constitution Number (a unique number, allocated sequentially as a substance is added to the Color Index).



Example:

The IUPAC name of the above dye is:

N-[(2-methylbenzene-4-sulphonic acid)-2-azo-1-naphthol-3- sulphonic acid]-*N*'-[(2-methoxybenzene)-2-azo-1-naphthol-3-sulphonic acid-6-]urea sodium salt

For example: Acid Yellow 1
 ↑ ↑ ↓
 Type of Dye Color type Number

11.3 Methods of dyeing

Dear student, you have learnt Colour and Constitution. Under this sub topic you learn about Methods of dyeing. Can you mention the common methods of dyeing? Let warm up your self with the following activities.



Learning task 11.3



a) Explain why methods of dyeing vary from one fabric to other.

Methods of dyeing or Method of application vary from one fabric to other.

For example

- ✓ If the class of the dye is acid, the dye is applied usually from neutral to acidic dyebaths
- ✓ If the class of the dye is basic, the dye is applied from acidic dyebaths
- ✓ If the class of the dye is vat, Water-insoluble dyes solubilized by reducing with sodium hydrogen sulfite, then exhausted on fiber and reoxidized and etc

The dyeing of fiber from an aqueous dye bath depends on the dye-fiber interaction.

- ✓ Depending on the nature of dye and the nature of fiber, the dye is fixed on to the fiber chemically or physically.
- ✓ Additives such as wetting agents, salts, carriers, retarders and others may be added to the dye bath along with the dye if required to facilitate the dyeing process.

11.4 Classification of dyes

Dear student, you have learnt Methods of dyeing. Under this sub topic you learn about Classification of dyes. Can you mention some of the major classification of dyes? Let warm up your self with the following activities.



Learning task 11.4



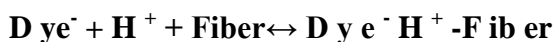
- a) Explain how dyes are classified
- b) Mention some of the common classes of dyes
- c) Compare and contrast the major classes of dyes
- d) Discuss the use of classifying dyes in to different groups

Dyes may be classified according to their chemical structure or by the method by which they are applied to the substrate. The dye manufacturers and dye chemists prefer the former approach of classifying dyes. The dye users, however, prefer the latter approach to of classification . Classification by application or usage is the principal system adopted by the *Color Index (C.I.)*.

11.4.1 Application and Classification of Dyes

i) Acid Dyes

Acid dyes are water-soluble anionic dyes, containing one or more sulfonic acid substituents or other acidic groups. An example of the class is Acid Yellow 36. Acid dyes are applied from acidic dye baths to nylon, silk, wool, and modified acrylics. They are also used to some extent for paper, leather, ink-jet printing, food, and cosmetics. The dyeing process is reversible and may be described as follows:



The ionic bonding between the dye and the fiber is the result of reaction of the amino groups on the fiber with acid groups on the dye. Generally the fastness of this dye depends on the rate with which the dye can diffuse through the fiber under the conditions of washing. Metal complex (cobalt or chromium) acid dyes are used mainly on wool for improved fastness.

ii) Azo Dyes

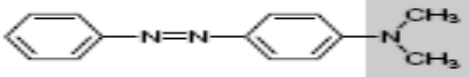
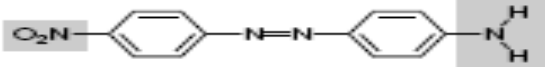
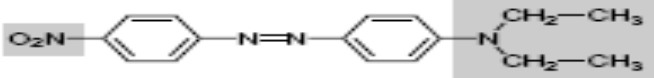
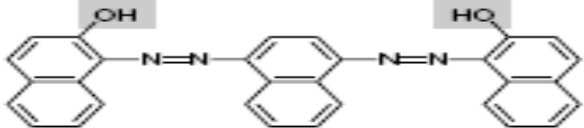
Azo dyes contain at least one **azo group (-N=N-)** attached to one or often two aromatic rings. They are produced on textile fibers (usually cotton, rayon and polyester) by diazotization of a primary aromatic amine followed by coupling of the resulting diazonium salt with an electron-rich nucleophile (azo coupling). A variety of hues can be obtained by proper choice of diazo and coupling components.

iii) Basic (Cationic) Dyes

Basic dyes are water-soluble and produce colored cations in solution. They are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic. They become attached to the fibers by formation of salt linkages (ionic bonds) with anionic groups in the fiber. They are used to dye paper, polyacrylonitrile, modified nylons, and modified polyesters. In solvents other than water, they form writing and printing inks. The

principal chemical classes are triaryl methane or xanthenes. Basic Brown 1 is an example of a cationic dye that is readily protonated under the pH 2 to 5 conditions of dyeing.

Table 11.1 Azo groups with color

Structure	Colour observed
	Yellow-green
	Yellow
	Red
	Blue

■ - Auxochrome

iv) Direct Dyes

Direct dyes are water-soluble anionic dyes, but are not classified as acid dyes because the acid groups are not the means of attachment to the fiber. They are used for the direct dyeing of cotton and regenerated cellulose, paper and leather. They are also used to dye union goods (mixed cotton, and wool or silk) and to a lesser extent nylon fiber. Most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines. The solubility of the dye in the dye bath is often reduced by adding common salt or Glauber's salt. The presence of excess sodium ions favors establishment of equilibrium with a minimum of dye remaining in the dye bath. Direct Orange 26 is a typical direct dye.

iv) Disperse Dyes

Disperse dyes are substantially water-insoluble nonionic dyes for application to synthetic hydrophobic fibers from aqueous dispersions. Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then form a solid solution. Dispersed dyes are primarily used for polyester and acetate fibers. Simple soluble azo, styryl

benzodi furanone, and insoluble anthraquinone are the most common disperse dyes. Disperse Yellow 3, Disperse Red 4, and Disperse Blue 27 are good examples of disperse dyes:

v) **Fiber-Reactive Dyes**

- These dyes react with the cellulosic fiber to form a covalent bond. This produces dyed fiber with extremely high wash fastness properties. Cotton, rayon, and some nylons are dyed by this relatively simple dye. An example of this type is the **Reactive Blue 5** dye. The principal chemical classes of fiber reactive dyes are:
- Azo, triphendioxazine, phthalocyanine, formazan and
- Anthraquinone.

vi) **Mordant Dyes**

Some dyes combine with metal salts (mordanting) to form insoluble colored complexes (lakes). These materials are usually used for the dyeing of cotton, wool or other protein fiber. The fiber is first treated with an aluminum, chromium and iron salt and then contacted with a lake forming dye (azo and anthraquinone derivatives). The metallic precipitate is formed in the fiber producing very fast colors highly resistant to both light and washing. Alizarin is the best-known anthraquinone derivative as an example of a mordant dye. The hydroxyl groups attached to anthraquinone nuclei are capable of reacting with metals in the mordant material (aluminum hydroxide) to form mordant dyes (aluminum "lake").

vii) **Sulfur Dyes**

Sulfur dyes are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent. These dyes are water-insoluble but they are soluble in their reduced form and exhibit affinity for cellulose. On exposure to air they are oxidized to reform the original insoluble dye inside the fiber. They are low cost and have good fastness to light, washings and acids. The actual structures of sulfur dyes are largely unknown although it is considered that they possess sulfur-containing heterocyclic rings.

viii) Vat Dyes

The vat dyes are insoluble complex polycyclic molecules based on the quinone structure (ketoforms). They are reduced with sodium hydrosulfite in a strongly alkaline medium to give soluble leuco forms that have a great affinity for cellulose. After the reduced dye has been absorbed on the fiber, the leuco forms are reoxidized to the insoluble keto forms. The dyeing produced in this way has high wash and light fastness. An example of a vat dye is VatBlue 4 (Indanthrene).

ix) Solvent Dyes

These dyes are water-insoluble but soluble in alcohols, chlorinated hydrocarbons, or liquid ammonia. They are used for coloring synthetics, plastics, gasoline, oils and waxes. The dyes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane dyes are also used. Perchloroethylene is the preferred solvent.

x) Fluorescent Brighteners

Fluorescent brighteners or fluorescent whitening agents (FWAs) are colorless to weakly colored organic compounds. These compounds are added to soaps and detergents to produce greater brilliance in laundry washings. FWAs are used for improving the appearance of recycled paper. An example of a FWAs is 4, 4'-bis (ethoxycarbonylvinyl) stilbene, which can be obtained by the reaction stilbene-4,4'-dicarbaldehyde with triethylphosphonoacetate in the presence of sodium methoxide.

xi) Food, Drug, and Cosmetic Dyes

Most synthetic and natural dyes commonly used in food, drug, and cosmetics are carefully controlled materials, regulated by the government agencies of different countries. These currently consist of very few (under 100) dyes and are listed in the approved list. Regulations list the approved color additives and conditions under which they may be safely used, including the amounts that may be used. The most frequently used synthetic dyes for food, drugs and cosmetics belong to azo, anthraquinone, carotenoid and triarylmethane chemical types.



Chapter summary



- Dyes are colored organic compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials
- The two major types of colorants produced today are dyes and pigments.
- Pigments do not interact with the substrate and hence do not destroy the crystal structure of the substrate
- Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance.
- The *Color Index* serves as a reference source for both the chemical structure and technical properties of dyes
- Dyes may be classified according to their chemical structure or by the method by which they are applied to the substrate.



Self test exercises



1. Dyes are colored organic compounds that are used to impart color to various substrates,
 - a) Explain the history of dye industry
 - b) Discuss the difference between dyes and pigments
- 2) Color Index serves as a reference source for the chemical structure and technical properties of dyes
 - a) Discuss the effect of structure on color observed
 - b) Explain how auxochromes and chromophores influence color intensity of a dye
3. Explain why methods of dyeing vary from one fabric to other.
4. Dyes may be classified according to their chemical structure or by the method by which they are applied to the substrate
 - a) Mention some of the common classes of dyes
 - b) Compare and contrast the major classes of dyes



Unit Introduction

Dear student, this chapter deals with Leather Industry. We will also discuss about Animal skins, Preparation of hides for tanning, Leather Tanning and Leather production processes, Vegetable tanning, Chrome tanning, Leather finishing, Role of enzymes in leather production and Environmental impacts of Leather Industry



Learning objective of the unit



Dear student, after reading through this unit and completion of the tasks and activities, you will be able to:

- Define Leather
- Define tanning
- Explain how skin is prepared for tanning
- Discuss briefly the process of Leather Tanning and Leather production
- Compare and contrast Vegetable tanning and Chrome tanning
- List the major steps that is used for leather finishing
- Explain the Role of enzymes in leather production
- Mention some of the Environmental impacts of Leather Industry

Dear student, the chemistry and engineering behind the leather industries are so complex that scientific control has developed comparatively slowly.

The skins and bones of animals and their products-leather, gelatin, glue-are mostly colloidal materials and have almost indefinable properties, about which too little is known. The raw skin consists of a number of different complex proteins which vary in structure in different animals and even vary in different parts of the same hide. The complexity of the art of leather manufacturing is increased by the large number of active substances that affect the skin – enzymes, bacteria, alkalis, acids, tannins, tannin substitutes, oils, fats, and salts.

Leather is a durable and flexible material created via the tanning of putrescible animal rawhide and skin, primarily cattle hide. It can be produced through different manufacturing processes, ranging from cottage industry to industry. Leather is made from animal skins or hides which have been chemically treated to preserve quality and natural beauty.

12.1 Animal skins

Dear student, you have learnt the complexity of the art of leather manufacturing is increased by the large number of active substances that affect the skin –enzymes, bacteria, alkalis, acids, tannins, tannin substitutes, oils, fats, and salts. Can you mention the difference between skin and hide? Let warm up your self with the following activities.



Learning task 12.1



- a) Define skin
- b) Explain the difference between skin and hide
- c) List some of the uses of skin

Animals skins as received by the tanner may be divided in three layers; the epiderms, the derma or corium, and the flesh. The epiderms, constituting about 1% of total skin, is the outer layer, and consists chiefly of the protein keratin. The hair, which grows through both the derma and epidermis, is also largely keratin. This layer is dense and chemically resistant, thus allowing the epidermis to be readily removed by chemical means. Hot water, however, causes a slow solubilization by hydrolysis of the collagen to produce gelatin. The elastin is not affected by this treatment. The flesh is an extraneous layer, mostly adipose tissue, which must be removed to ensure tannin penetration on both sides of the corium

12.2 Preparation of skins for tanning

Dear student, you have learnt Animals hides received by the tanner may be divided in three layers; the epidermis, the derma or corium, and the flesh. Under this sub content you learn how hides are prepared for tanning. Do you know tanning? Let warm up your self with the following activities.



Learning task 12.2



- a) Define Tanning
- b) Explain how hides are prepared for tanning
- c) Discuss the advantage of Preservation and Disinfection of hides
- d) Explain how the hair is removed from epidermis of animal hides

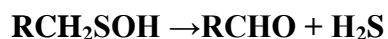
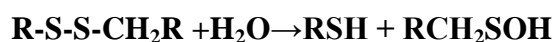
Dear student, the first step in the tanning process is the inspection of the hides for defects as they come into the tannery and the cutting off of ears and ends. The next step is the cleansing of hides to remove dirt, manure, and salt in order to restore the hide to a natural soft hydrated state by paddle washing, drum washing, or soaking in vats. The soaking and washing of the hides are quite important, because if moisture is not restored, the hide will not respond properly to the different tanning operations. Small amounts of sodium polysulfide and surfactants are added, which greatly accelerate the soaking.

Disinfectants are used in soaks to offset bacteria present from delayed or inadequate cure. Liming is a means of loosening and removing the epidermis and hair from the hide and is usually done in paddles, drums, and pits.

The hides are tied or hooked together and placed in vats containing water with 10% of the weight of the hides in lime and 2% of the hide weight in sodium sulfide, which acts as accelerating agent. Dimethyl amine, sulfhydrate, and cyanide salts are also used as accelerating, or sharpening, agents. The hides are moved ahead daily in a series consisting of three to seven vats,

remain in each one day, and then enter a fresher lime vat. The epidermis and hair are composed chiefly of keratin.

Keratin is a protein containing a cystine residue which is easily attacked by alkali. Lime attacks the disulfide link of the keratin of the epidermis and the cortical layer and the hair. This softens the hair and removes the epidermis. This action may be represented as:



After the hides have passed through this process, they are usually placed in a vat of warm water, which tends to relax them and permits the easier removal of the hair in a dehairing machine. The skins are brought into contact with a roller set with dull knife blades, which rub off the loose hair and epidermis. Bating has been one of the most mysterious processes carried out in the tannery and by far the most unpleasant.

12.2.1 Preservation and Disinfection of skins

Since raw skins decay rapidly, some method of preservation must be used to arrest bacterial action and consequent hide disintegration. Tannery experience with domestic hides has demonstrated superiority of brine curing, to which a bactericide has been added, over those cured by the conventional green-salt method. Curing is more rapid and uniform; affords greater protection prior to tanning; practically eliminates "salt stains"; requires no washing of hides before "soaking back"; and produces leather of plumper grain.

In salt curing, standard domestic practice piles the hides flesh side up in alternate layers with salt. These packs are arranged for proper drainage of the brine. This method of curing requires a minimum of 3 or 4 weeks at about 13°C, during which the hide loses part of its moisture by dehydration and gains weight through salt absorption. The loss is the greater, and the overall difference is termed the "shrink". Many irregularities in the leather may be traced to careless curing and storing.

12.3 Leather Tanning and Leather production processes

Dear student, you have learnt Animals hides received by the tanner may be divided in three layers; the epidermis, the derma or corium, and the flesh. Under this sub content you learn how hides are prepared for tanning. Do you know how a leather prepared for tanning? Let warm up your self with the following activities.



Learning task 12.3



- a) Define Leather Tanning
- b) Explain how hides are prepared for tanning
- c) Discuss the advantage of Preservation and Disinfection of hides
- d) Explain how hair is removed from epidermis of animal hides
- e) List the fundamental sub-processes in the leather manufacturing process

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer.

The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the U. S. are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents.

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. The leather manufacturing process is divided into three fundamental sub-processes:

- preparatory stages,
- tanning and,
- crusting.

All true leathers will undergo these sub-processes. A further sub-process, surface coating can be added into the leather process sequence but not all leathers receive surface treatment. Since many

types of leather exist, it is difficult to create a list of operations that all leathers must undergo. The **preparatory stages** are when the hide/skin is prepared for tanning.

Preparatory stages may include:

- preservation,
- soaking, liming, unhairing, fleshing, splitting, reliming, deliming, bating, degreasing, frizing, bleaching, pickling, and depickling.

Tanning is the process which converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications. The principal difference between raw hides and tanned hides is that raw hides dry out to form a hard inflexible material that when re-wetted (or wetted back) putrefy, while tanned material dries out to a flexible form that does not become putrid when wetted back.

Many different tanning methods and materials can be used; the choice is ultimately dependent on the end application of the leather. The most commonly used tanning material is **chromium**, which leaves the leather, once tanned, a pale blue color (due to the chromium); this product is commonly called "**wet blue**". The hides once they have finished pickling will typically be between pH 2.8 and 3.2.

At this point, the hides would be loaded in a drum and immersed in a float containing the tanning liquor. The hides are allowed to soak (while the drum slowly rotates about its axle) and the tanning liquor slowly penetrates through the full substance of the hide. The pH of the leather when chrome tanned would typically finish somewhere between 3.8 and 4.2

Leather production uses raw material in the form of: Cow and buffalo hides and goat and sheep Skins as the raw material and a number of imported chemicals. Leather manufacturing involves following major steps:

- | | |
|------------------------|--------------------------|
| 1. Pre-Process | 4. Wet Finishing Process |
| 2. Pre-Tanning Process | 5. Dry Machining |
| 3. Tanning Processes | 6. Finishing |

In pre-processing skins/hides are received and salt is applied on the flesh side of the skins/hides. Skin trimming is done to remove unwanted parts. After pre-processing, pre-tanning process starts with the soaking process in which skin are made flaccid by soaking them in water. After soaking hair is removed, lime is used to make hair loose. Unwanted flesh is removed with the help of fleshing machines after liming process. To prepare limed skin for tanning, the skins are delimed using Ammonium Sulphate and then skins are washed. Bating is done for further purification of hide. After that degreasing is done with the help of detergents.

Tanning process starts with pickling which is the treatment of skin with acids and salts to bring it to desired level of pH. Tanning process stabilizes the collagen network of skin. After tanning skins are called wet blue and are stored for sometime and then they are sorted out according to quality. If hides of cows or buffaloes are being used for leather manufacturing, then after this they are sliced to give desired thickness. This process is not carried out on the skins of goats or sheep. After this the hair sides of the wet blue are shaved to give the desired thickness.

In order to give desired softness, color, strength, and quality to the leather wet blue skins are processed further through wet finishing process. Fat liquoring process is carried out to impart desired softness and dyeing is to give it a color. After wet process different drying processes are carried out to dry the processed leather. These processes consist of smaying/setting, vacuum drying, stacking/toggling, buffing/shaving, trimming, pressing, and segregation of the leather. Finally finishing processes are carried out to impart durability and beauty to the leather.

The chemicals used in the leather industry can be divided into three broad categories:

1. Pre-tanning Chemicals
2. Tanning Chemicals
3. Finishing Chemicals

Pre-tanning chemicals are used to clean and prepare skins for the tanning process and they are mostly washed away with the wastewater. Like tanning chemicals finishing chemical also get discharged into wastewater. Only those chemicals are fully retained which are applied as surface coating. A large amount of water is used in whole manufacturing process.

In tanning process water is used as carrier to facilitate different chemical reactions and after completion of process the water leaves the system as wastewater in the same quantity as added to the system.

- Ground water is mainly used as processing water.
- Tanning chemicals react with the collagen fibers of the skin to convert them into leather.
- These chemicals are retained in the skin but a good amount of these is discharged into wastewater.
- Chrome sulphate is the basic tanning chemical.
- Apart from being expensive, Chrome sulphate is also a serious pollutant.
- Finishing chemicals are used to impart certain properties to the leather like softness, color, appearance and etc.

a) Curing

Animal skins or hides are first "cured," a process which involves salting and/or drying the hide once it's been stripped from the animal. Because this step needs to be performed almost immediately upon removal from the animal, it often takes place inside the meat-packing industry or at a nearby factory. Hides can be cured in one of two ways:

i) Wet-Salting (wet-curing) - is done by salting the hide and then piling many skins together until they form a moist bunch. They are then left to cure for one month, so that the salt can completely be absorbed into the skin.

ii) Brine-curing - is more common than wet-salting, as it's considered a faster, easier method. During brine curing, hides are positioned carefully in vats and smothered with a mixture of salt and disinfectant. After 10-16 hours, the skins are completely cured and ready to move on to the next stage.

b) Soaking - once the hides have been cured, they are then soaked in water for several hours to several days. The water helps to rid the skin of salt, dirt, debris, blood and excess animal fats.

c) Liming - after being soaked, the hair and epidermis is removed by treating hides with a mixture of sodium sulphide and lime solutions.

- d) Flesh removal** - after soaking, animal hides are moved through a machine which strips the flesh from the surface of the hide.
- e) Hair removal** - the hides are then transported to a large vat, where they are immersed in a mixture of lime and water, which loosens the hair from the skin. After a 1-10 day soak, the hair is mechanically removed from the hide.
- f) Scudding** - stray hairs and fat which were missed by machine are removed from the hide with a plastic tool or dull knife in a process known as "scudding." Scudding is done by hand.
- g) Delimiting** - after the hair and debris has been cleaned from the skin, hides are delimited in a vat of acid. After the lime has been pulled from the skin, hides are treated with enzymes, which smooth the grain of the leather and help to make the resulting product soft and flexible
- h) Splitting** - the hide is split into layers; the grain layer (top) is used in the manufacture of 'Top Grain Leather' (premium upholstery, clothing, etc) the lower split is used for polyurethane protected automotive upholstery and the flesh split (bottom) is sold to other manufacturers for the production of suede, or to the food industry as a source of collagen.

12.4 Vegetable Tanning

Dear student, you have learnt Leather Tanning and Leather production processes under this sub content you learn how hide Vegetable Tanning. Do you know how hides are tanned using vegetable? Let warm up your self with the following activities.



Learning task 12.4



- a) Discuss how a skin tanned using Vegetable
- b) Explain the properties of a leather which tanned by vegetable
- c) Compare and contrast vegetable tanning to Chrome tanning

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair

follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist.

The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine.

- ✓ Deliming is then performed to make the skins receptive to the vegetable tanning.
- ✓ Bating, an enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch, and flexibility to the leather.
- ✓ Pickling may also be performed by treating the hide with a brine solution and sulfuric acid to adjust the acidity for preservation or tanning.

In the vegetable tanning process, the concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds. It usually takes 3 weeks for the tanning material to penetrate to the center of the hide. The skins or hides are then wrung and may be cropped or split; heavy hides may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins.

Materials such as lignosulfate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smooth and dry and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, coloring, fatliquoring, or finishing. Leather may be dried by any of five common methods. Air drying is the simplest method.

The leather is hung or placed on racks and dried by the natural circulation of air around it. A toggling unit consists of a number of screens placed in a dryer that has controlled temperature and humidity. In a pasting unit, leathers are pasted on large sheets of plate glass, porcelain, or metal and sent through a tunnel dryer with several controlled temperature and humidity zones.

In vacuum drying, the leather is spread out, grain down, on a smooth surface to which heat is applied. A vacuum hood is placed over the surface, and a vacuum is applied to aid in drying the

leather. High-frequency drying involves the use of a high frequency electromagnetic field to dry the leather. Several tanning processes transform hides and skins into leather:

Vegetable-tanned leather is tanned using tannin and other ingredients found in vegetable matter, tree bark, and other such sources. It is supple and brown in color, with the exact shade depending on the mix of chemicals and the color of the skin. It is the only form of leather suitable for use in leather carving or stamping.

Vegetable-tanned leather is not stable in water; it tends to discolor, and if left to soak and then dry it will shrink and become less supple and harder. In hot water, it will shrink drastically and partly gelatinize, becoming rigid and eventually brittle. Boiled leather is an example of this where the leather has been hardened by being immersed in hot water, or in boiled wax or similar substances.

12.5 Chrome Tanning

Dear student, you have learnt Leather Vegetable Tanning under this sub content you learn Chrome Tanning. Do you know how hides are tanned using chrome? Let warm up your self with the following activities.



Learning task 12.5



- a) Discuss how a skin tanned using chromium
- b) Explain the properties of a leather which is tanned by chromium
- c) Compare and contrast vegetable tanning to Chrome tanning

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned.

The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring are usually

performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheep skin.

For example, Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised.

Following tanning, the chrome tanned leather is piled down, wrung, and graded for the thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i. e., shoe leather) the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

12.6 Leather Finishing

Dear student, you have learnt Leather Chrome Tanning; under this sub content you learn Leather Finishing. Do you know how Leather Finishing can be performed? Let warm up your self with the following activities.



Learning task 12.6



- a) Mention how leather finishing can be performed
- b) Compare and contrast one method of leather finishing to other methods

Leathers may be finished in a variety of ways:

- buffed with fine abrasives to produce a suede finish;
- waxed, shellacked, or treated with pigments, dyes, and
- resins to achieve a smooth, polished surface and the desired color; or
- lacquered with urethane for a glossy patent leather.

Water-based or solvent-based finishes may also be applied to the leather. Plating is then used to smooth the surface of the coating materials and bond them to the grain. Hides may also be embossed.

12.7 Role of enzymes in leather production

Dear student, you have learnt how Leather Finishing can be performed; under this sub content you learn the Role of enzymes in leather production. Can you mention some of the roles of enzymes in leather production? Let warm up your self with the following activities.



Learning task 12.7



a) Mention the major roles of enzymes in leather production

Enzymes like proteases, lipases and amylases have an important role in the soaking, dehairing, degreasing, and bating operations of leather manufacturing. Proteases are the most commonly used enzymes in leather production. The enzyme used should not damage or dissolve collagen or keratin, but should be able to hydrolyze casein, elastin, albumin and globulin-like proteins, as well as non-structured proteins which are not essential for leather making. This process is called bating. Lipases are used in the degreasing operation to hydrolyze fat particles embedded in the skin. Amylases are used to soften skin, to bring out the grain, and to impart strength and flexibility to the skin. These enzymes are rarely used.

12.8 Environmental impacts of Leather Industry

Dear student, you have learnt the Role of enzymes in leather production; under this sub content you learn Environmental impacts of Leather Industry. Can you mention some of Environmental impacts of Leather Industry? Let warm up your self with the following activities.



Learning task 12.8



- a) Mention the major categories of waste that are emitted by leather industry
- b) Explain the source of chromium emission in Leather industry
- c) List possible remedial measures that can be used to lessen the environmental impact of tanneries.

All the three categories of waste: solid, liquid, and gaseous, are emitted by the leather industry in the form of:

1. Solid Wastes
2. Wastewater
3. Air Emissions

12.8.1 Emissions and Controls

There are several potential sources of air emissions in the leather tanning and finishing industry. Emissions of VOC may occur during finishing processes, if organic solvents are used, and during other processes, such as fat liquoring and drying. If organic degreasing solvents are used during soaking in suede leather manufacture, these VOC may also evaporate to the atmosphere.

Many tanneries are implementing water-based coatings to reduce VOC emissions. Control devices, such as thermal oxidizers, are used less frequently to reduce VOC emissions. Ammonia emissions may occur during some of the wet processing steps, such as delimiting and unhairing, or during drying if ammonia is used to aid dye penetration during coloring. Emissions of sulfides may occur during liming/unhairing and subsequent processes. Also, alkaline sulfides in tannery wastewater can be converted to hydrogen sulfide if the pH is less than 8.0, resulting in release of this gas.

Particulate emissions may occur during shaving, drying, and buffing; they are controlled by dust collectors or scrubbers. Chromium emissions may occur from chromate reduction, handling of basic chromic sulfate powder, and from the buffing process. No air emissions of chromium occur during soaking or drying. At plants that purchase chromic sulfate in powder form, dust containing trivalent chromium may be emitted during storage, handling, and mixing of the dry chromic sulfate.

12.8.2 Remedial measures

Several remedial measures are suggested to lessen the environmental impact of tanneries.

- In large and medium sized tanneries environmental management system must be developed.
- Staff should be trained for occupational health and safety.
- Gaseous masks must be provided for workers in order to prevent inhalation of fumes.
- Proper arrangement must be made to stop use of tanneries solid waste to make poultry feed.
- Improvement in drainage system is needed to avoid the formation of hydrogen Sulphide in the tannery.
- Many options are available for reuse of chrome, discharged in the tanning effluent.
- This includes direct recycling of chrome tanning float, recycling of chrome after precipitation, and use of tanning products that improve the exhaustion rate.



Chapter Summary



- **Leather** is a durable and flexible material created via the tanning of putrescible animal rawhide and skin, primarily cattle hide.
- Leather is made from animal skins or hides which have been chemically treated to preserve quality and natural beauty.
- the first step in the tanning process is the inspection of the hides for defects The next step is the cleansing of hides to remove dirt, manure, and salt in order to restore the hide to a natural soft hydrated state by paddle washing, drum washing, or soaking in vats.
- Disinfectants are used in soaks to offset bacteria present from delayed or inadequate cure.
- "Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. The leather manufacturing process is divided into three fundamental sub-processes:
 - ✓ preparatory stages,
 - ✓ tanning and,
 - ✓ crusting.
- Preparatory stages may include:
 - ✓ preservation,
 - ✓ soaking, liming, unhairing, fleshing, splitting, reliming, deliming, bating, degreasing, frizing,bleaching, pickling, and depickling.
- Tanning is the process which converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications.
- **Vegetable-tanned leather** is tanned using tannin and other ingredients found in vegetable matter, tree bark, and other such sources.
- Chrome tanning is a tanning process, that used chromium salt, which leaves the leather, once tanned, a pale blue color (due to the chromium); this product is commonly called "**wet blue**".
- Enzymes like proteases, lipases and amylases have an important role in the soaking, dehairing, degreasing, and bating operations of leather manufacturing
- Solid, liquid, and gaseous wastes are the major waste types emitted by the leather industry
- Some of the common remedial measures that can be used to lessen the environmental impact of tanneries are:

- ✓ In large and medium sized tanneries environmental management system must be developed.
- ✓ Staff should be trained for occupational health and safety.
- ✓ Improvement in drainage system is needed to avoid the formation of hydrogen Sulphide in the tannery.
- ✓ direct recycling of chrome tanning float, recycling of chrome after precipitation, and use of tanning products that improve the exhaustion rate.



Self test exercises



1. Explain the difference between skin and hide
2. Tanning is the process which converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications.
 - a) Explain how hides are prepared for tanning
 - b) Discuss the advantage of Preservation and Disinfection of hides before tanning
 - c) Explain how the hair is removed from epidermis of animal hides
3. "Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather.
 - a) List the fundamental sub-processes in the leather manufacturing process
4. The most common types of leather tanning are Vegetable tanning and Chrome tanning
 - a) Compare and contrast vegetable tanning to Chrome tanning
 - b) Mention how leather finishing can be performed
5. Mention the major roles of enzymes in leather production
- 6) The major categories of waste that are emitted by leather industry are solid waste, wastewater and gaseous substances; list possible remedial measures that can be used to lessen the environmental impact of tanneries.